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Review of In-Place Treatment Techniques for Contaminated Surface Soils
Volume 1. Technical Evaluation

JRB Associates, Inc., McLean, VA

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This two-volume report presents information on in-place treatment technologies applicable to contaminated soils at shallow depths. This volume discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2 provides background information and relevant chemical data.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives.

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VOLUME 1:
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FOREWORD

This is one of a series of reports being published to implement CERCLA, otherwise known as Superfund legislation. These are documents explaining the hazardous response program and, in particular, the technical requirements for compliance with the National Contingency Plan (NCP), the analytical and engineering methods and procedures to be used for compliance, and the background and documenting data related to these methods and procedures. The series may include feasibility studies, research reports, manuals, handbooks, and other reference documents pertinent to Superfund.

This two-volume report presents information on in-place treatment technologies applicable to contaminated soils at shallow depths. This volume discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2 provides background information and relevant chemical data, and is available from NTIS.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives.

ABSTRACT

This two-volume report presents information on in-place treatment technologies applicable to contaminated soils less than 2 feet in depth. Volume 1 discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2, available through NTIS, provides background information and relevent chemical data.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives.

Technologies in the five groups mentioned above are discussed according to the following categories of information:

- description,
- wastes amenable to treatment,
- status of technology,
- ease of application,
- potentially achievable level of treatment,
- reliability of method,
- secondary impacts,
- equipment and exogenous reagents,
- information requirements, and
- sources of information.

This report was submitted in partial fulfillment of Contract Nos. 68-03-3113 and 68-01-6160 (Work Order 12) by Utah State University and Arthur D. Little, Inc., respectively, under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period May, 1982 to September, 1984, and work was completed as of April 1, 1984.

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EXECUTIVE SUMMARY

PURPOSE AND SCOPE

The purpose of this report is to provide state-of-the-art information on in-place treatment technologies for soils contaminated to a shallow depth. Such situations are commonly encountered when the source of contamination is at or near the soil surface. Examples include leakage from unpaved drum storage areas, spills in truck and rail transport, spills in transfer of chemicals, and leakage from shallow lagoons or burial pits.

The in-place technologies discussed have the potential for attenuating, extracting, immobilizing, degrading, or reducing the volatilization of both inorganic and organic soil contaminants. The particular application methods emphasized in this report are generally limited to contaminated soils that lie above the water table. With different application methods, not discussed in detail in this report, the basic technologies can be adapted to treatment of contaminants in the saturated zone.

This report has been divided into two volumes. Section 2 of Volume 1 provides a guide for selection of in-place treatment technologies. Section 3 provides a discussion of each in-place treatment technology, including process description, information requirements for application of the technology, wastes amenable to treatment, current status of the technology, ease of application, potentially achievable levels of treatment, reliability of the technology over the long term, secondary impacts, and equipment materials required to implement the technology. Section 4 discusses engineering methods for modifying the oxygen content, moisture content, nutrient content, pH and temperature of the soil to optimize the effectiveness of in-place treatment. In addition, data for estimating the costs of implementing in-place treatment are provided in Section 4 and in an appendix on cost information.

Background information for characterization and evaluation of immobilization, degradation, and volatilization processes in waste/soil systems is provided in Volume 2 of the report, available through NTIS.

SELECTION PROCESS FOR IN-PLACE TREATMENT TECHNOLOGY

The technologies discussed in this report are potentially applicable for immediate removal, planned removal, and remedial action as defined in the National Contingency Plan (NCP). They could be particularly cost-effective in situations in which contamination has not yet reached groundwater, but would be expected to do so if no action were taken. They also have the potential for controlling or preventing further migration of contaminants to groundwater. In the latter case, in-place treatment of near-surface soils might be sufficient in and of itself to achieve remedial objectives, or it might be used in conjunction with other source control and offsite remedial actions directed at containment or cleanup of already contaminated groundwater.

The procedure for selecting appropriate remedial action technologies (including in-place treatment technologies) is specified in the National Contingency Plan. The prescribed steps are as follows:

- Preliminary assessment (scoping) — Determination on the basis of available data of the possible need for remedial response.

- Remedial investigation — Gathering of sufficient information, generally through field sampling and monitoring, to determine the nature and extent of both the problem and the remedial action that may be necessary.

- Setting of objectives — Defining the goal(s) or desired end-result(s) of the remedial program. In general, objectives will include an environmental goal (e.g., reduce exposure via the direct contact, air, groundwater, and surface water pathways to some level of acceptability) and a cost effectiveness component (e.g., to achieve the environmental goal(s) using the least cost alternative that is technically feasible and reliable).

- Identification of alternatives with potential for meeting the environmental goal(s) — the identification should be as comprehensive as possible so that the most cost-effective alternative is not overlooked.

- Screening alternatives — Evaluation of the technical effectiveness, reliability, engineering practicality, costs (capital, operating, and maintenance), and environmental impacts of implementing each alternatives.

- Refinement and detailed specification of alternatives that pass screening —Detailed cost estimation, including distribution of costs over time; specification and evaluation of an engineering implementation plan; detailed assessment of how well each alternative meets the remedial objectives; and detailed analysis of any adverse environmental impacts, mitigation measures, and associated costs.

- Selection of the most cost-effective alternative — This will generally be the lowest cost alternative of those analyzed in detail that meets the objectives of the remedial program.

When the remedial investigation shows contamination of near-surface soils as contributing to risk, Table 2-1 should be consulted to identify the in-place technologies that might be appropriate. In the identification step, the primary consideration is the chemical nature of the contaminants of concern. In particular, some technologies are designed primarily to control the release of heavy metals, while others are designed primarily to control the release of organics. When both types of contaminants are of concern, the possibility of combining two or more in-place technologies to meet remedial objectives should be considered.

SPECIFIC IN-PLACE TREATMENT TECHNIQUES

There are five major categories of in-place treatment techniques. These are:

- Extraction,
- Immobilization,
- Degradation,
- Attenuation, and
- Reduction of volatilization.

Specific technologies within each category are discussed briefly below.

EXTRACTION (SOIL FLUSHING)

Extraction is the washing of contaminants from the soil with a suitable solvent such as water, or other aqueous or non-aqueous solutions. The method is potentially applicable to all types of soil contaminants, provided that a suitable non-polluting solvent can be found. Effects of the solvent on the physical, chemical, and biological properties of the soil need to be evaluated. Furthermore, a system for profusing the contaminated area with solvent and for capturing the elutriate needs to be designed. This might involve flooding the site and collecting the elutriate in a series of shallow well points or subsurface drains, or appropriate placement of recharge and discharge wells. After treatment, the elutriate might be discharged to a receiving water body or sewer, or it might be recycled through the contaminated area. This technology derives from the mining industry, where it has been used for in-place extraction of metal values from ores.

IMMOBILIZATION

Immobilization includes a wide range of in-place treatment technologies designed to reduce the rate of release of contaminants from the soil so that resultant concentrations along pathways of exposure are held within acceptable limits. The primary immobilization mechanisms are sorption, ion exchange, and precipitation. Sorption is potentially applicable to both organic and inorganic contaminants. Ion exchange is applicable to organic and inorganic cation and anion species. Precipitation is limited, for most practical purposes, to heavy metal contaminants.

Sorption of Heavy Metals

Heavy metal contaminants in soil may be immobilized by mixing the contaminated soil with a good adsorbent, or mixture of adsorbents, for the metals present, or with a metal complexing agent, such as tetren, that binds the metal into a complex that strongly adsorbs to soil. The adsorbent, or complexing agent, may be mixed into the soil with conventional power implements or tillers. Suitable adsorbents for heavy metals include various agricultural products and by-products, such as straw, sawdust, peanut hulls, bark, and activated carbon. For maximum adsorption efficiency, the pH of the soil generally needs to be above 6.5. To maintain a high pH, lime can be mixed into the soil with the adsorbent. The amount of adsorbent added must be sufficient to tie up the releasable heavy metals, and periodic reliming may be necessary to maintain the treated system at a pH above 6.5.

Tetren-metal complexes are strongly adsorbed to soil clays. For contaminated soils rich in clays, mixing of tetren (and lime, if the soil is acidic) into the contaminated area may be sufficient to achieve immobilization. If the contaminated soils are of low clay content, a combination of tetren, clay materials, and lime (if necessary) may be used. Tetren generally forms 1:1 complexes with metals and, hence, should be added in amounts slightly in excess of the number of moles of heavy metal contaminants present.

Sorption of Organics

The distribution of an organic chemical between soil and infiltrating precipitation at equilibrium is directly proportional to the fraction of organic carbon in the soil matrix. Therefore, addition of organic matter can increase the sorption capacity of the soil, and can be particularly effective for soils with low organic carbon content, such as sand and gravel. Possible sorbents include sewage sludge, agricultural products and by-products, organic soil materials, such as soils of the Histosol soil order, and activated carbon. The sorbents may be mixed into contaminated surface soils using conventional power implements and tillers.

Ion Exchange

Certain clays, synthetic resins, and zeolites have the capacity to release ions of one type and to preferentially adsorb ions of another type at the vacated lattice position (i.e., to exchange one type of ion for another). Cation exchangers have replaceable cations,and anion exchangers have replaceable anions.

Increasing the clay content of a soil can increase its capacity to immobilize cationic compounds. The cationic exchange capacity (CEC) of a soil is defined as the number of milli-equivalents of exchangeable ions per hundred grams dry weight of soil. Clays tend to have the highest CEC values among natural soils, and typically exchange calcium ions for cations of heavy metals or organics (see Table 3-7).

Synthetic resins have been developed that carry either exchangeable cations (e.g., Chelex 100) or exchangeable anions (e.g., Dowex 1-X8).

Zeolites are a family of crystalline-hydrated alumino silicates with high selectivity and capacity for adsorption of heavy metal cations. Zeolites are stable over the pH range of 6-12, but begin to degrade around pH 4-5 and below. Therefore, zeolites should be used only in alkaline or limed soils where the pH is maintained above 6.

Precipitation of Heavy Metals

The addition of sulfides, carbonates, phosphates, and hydroxides to metal-contaminated soils can immobilize metals by precipitation of a highly insoluble compound. Precipitating agents that may be mixed into the soil by standard agricultural techniques include lime for hydroxide precipitation, limestone for carbonate precipitation, trebel superphosphate for phosphate precipitation, and calcium sulfide or sodium sulfide for sulfide precipitation. The use of phosphate should be avoided if arsenic is present in the soil matrix, because of the potential for the formation and release of arsenate into infiltrating precipitation. Under some conditions, heavy metals may form soluble phosphate, carbonate, and hydroxide complexes that are more mobile than the free metal ions. By controlling the rate of addition of precipitating reagents and the pH of the contaminated soil system, it should be possible to optimize precipitation over a complex formation.

In-place precipitation of sulfides presents special complications in soil systems. The heavy metal sulfides are generally the least soluble of the heavy metal compounds. While the solubilities of metal sulfides decrease with increasing pH (except for arsenic, which precipitates only at pH 5), metal sulfides have very low solubilities, even at a pH as low as 4. Some heavy metals form soluble sulfide complexes that may be more mobile in the environment than the free metal ion. Controlled addition of sulfide reagent, controlled pH, and thorough mixing of the contaminated soil with the precipitating reagent can help to favor precipitation over soluble complex formation. More serious over the long term is the potential for oxidation of the precipitated sulfides to form soluble metal sulfates under aerobic soil conditions. Maintenance of a high soil pH is particularly important, since acid conditions will not only dissolve the metals, but also lead to the release of hydrogen sulfide. The latter is a highly toxic gas, and the odor, even if concentrations are below toxic thresholds, can result in a major community relations problem.

CHEMICAL DEGRADATION

Oxidation, reduction, and polymerization reactions may be carried out in-place to transform soil contaminants into less toxic or less mobile products.

Oxidation

Chemical oxidation of organic contaminants with half-wave potentials less than the redox potential (0.8 volt) of a well-aerated soil can be oxidized in-place in the presence of clay catalysts. This method is conceptual, and the oxidation products are not necessarily less toxic or less mobile than the original contaminants. As previously discussed, increasing the clay content of surface soils can aid in immobilization of contaminants. Clay-catalyzed oxidation of organics may be an additional benefit, or an undesired side effect, depending upon the products of oxidation. These should be investigated in laboratory or field treatability studies undertaken to develop design parameters for in-place treatment with clay.

Introduction of chemical oxidants into the soil system is another method for promoting the oxidation of organics. Possible oxidizing agents include ozone or hydrogen peroxide. The agents may be applied in water solutions directly onto the soil surface, injected into the subsurface, or introduced through injection wells. Since oxidants are relatively non-selective and may act on natural organics in the soil as well as organic contaminants, laboratory and field treatability studies would be required to assess the reactions that occur and to develop data for design of a full-scale treatment system if results are favorable.

Reduction

In-place reduction reactions may be brought about by the addition of reducing agents to the contaminated soil. Possible reagents include catalyzed metal powders of iron, zinc or aluminum, for example, or sodium borohydride. These reagents have been shown to degrade toxic organic constituents, although there have been very few demonstrations of in-place treatment of contaminated soils. Catalyzed metal powders can be applied to the soil surface and mixed into the contaminated soil with conventional agricultural equipment. Sodium borohydride can be applied in an alkaline water solution via irrigation, subsurface injection, or injection wells.

Hexavalent chromium is highly toxic and mobile in soils, generally in the form of a chromate ion. Trivalent chromium, the reduced form, is less toxic and readily precipitated by hydroxides over a wide pH range. Hexavalent chromium is readily reduced in natural soils. Mixing of ferrous iron, leaf litter, or acid compost into the surface soils can assist in the conversion. Liming of the soil once reduction is complete will precipitate trivalent chromium hydroxide compounds.

Hexavalent selenium, as selenate, is also highly soluble and mobile in soils. Selenates are readily reduced in natural soils to elemental selenium, which is virtually immobile, and also to selenites. The solubility and potential leachability of selenites increases with increasing pH. Hence the high pH that is generally required to immobilize other heavy metal contaminants could result in the release of selenium if any is present.

Polymerization

If a soil is contaminated with polymerizable organics such as styrene, vinyl chloride, isoprene, acrylonitrile, or methyl methacrylate, mixing of iron and sulfates into the contaminated area may catalyze an in-place polymerization reaction. The polymers are commonly less toxic and less mobile than the monomers from which they are formed. Generally, a 2:1 ratio of volume of catalysts and activator to volume of contaminant is required. The catalysts and activator are generally applied separately, and a wetting agent added to promote rapid and uniform dispersion of solutions through the contaminated area. The technical feasibility of the method and parameters for design of a full-scale system would need to be established by a combination of laboratory bench-scale and pilot field demonstrations.

BIODEGRADATION

Biodegradation, as the term is used here, refers to the breakdown of organic compounds in soils by the action of micro-organisms such as bacteria, actinomycetes, and fungi. Treatment generally consists of optimizing conditions of pH, temperature, soil moisture content, soil oxygen content, and nutrient concentration to stimulate the growth of micro-organisms that will feed on the particular contaminants present. Alternatively, genetically engineered organisms may be added to the soil system and conditions established within the soil to optimize their growth. Optimum conditions of application generally need to be established in laboratory bench-scale studies and small field pilot test spots. Some of the hazardous constituents present in a contaminated soil may be most readily biodegraded under aerobic conditions, while others are more readily degraded under anaerobic conditions. Treatment might therefore consist of alternate aerobic and anaerobic cycles.

While generally biodegradation is used as a detoxification mechanism for organic contaminants in soil, some micro-organisms will also interact with metallic species. For example, aerobic heterotrophic bacteria oxidize arsenite to arsenate. Further treatment with ferrous sulfate would then immobilize the arsenic in the form of highly insoluble ferric arsenate.

PHOTOLYSIS

Photochemical reactions require the absorption of light energy, generally from sunlight in natural systems. Since light does not penetrate very far into soils, photodegradation of soil contaminants is limited to soil surfaces. The addition of proton donors in the form of polar solvents, such as methanol, can enhance surface photodegradation of soil contaminants. For example, photolysis of dioxin (TCDD) on soil surfaces has been reported in the presence of methanol. Photodecomposition of PCBs at soil surfaces has been reported in the presence of triethylamine as a proton donor.

ATTENUATION

Attenuation is the mixing of contaminated surface soil with clean soil, using conventional power implements or tillers, so that the concentrations of hazardous components in the mixture are reduced to acceptable levels. Although potentially applicable to any type of waste, guidelines for acceptable concentration levels in surface soils are available only for heavy metals. The amount of clean soil required to assure that the mixture lies within an acceptable range is a practical limitation that needs to be evaluated.

REDUCTION OF VOLATILIZATION

If soil contaminants are volatile, and the air transport pathway could lead to adverse exposure, it may be important to suppress volatilization. This could have the added benefit of retaining compounds within the soil system for a long enough time to allow for in-place treatment by one of the mechanisms described above. The most practical method of suppressing volatilization is to reduce the soil vapor pore volume through which the transport of vapors occurs. This can be done by compaction or addition of water to reduce the air-filled pore spaces within the soil relative to the water-filled pore spaces. Another technique is to decrease the temperature of the soil, since vapor pressure of volatile constituents generally decreases with decreasing temperature.

METHODS FOR IMPLEMENTATION OF IN-PLACE TREATMENT

The in-place methods discussed in this report have many elements in common. Most involve application of absorbents or reagents and thorough mixing with the contaminated soil. Many involve liming for pH control and adjustment of the moisture content of the soil to optimize conditions of treatment.

Solid or semi-solid agents are typically applied to the soil surface by means of spreaders that may be truck-mounted, hitch-mounted, or tractor-drawn. Liquids can be applied with hydraulic sprayers or subsurface injectors. Mixing of treatment agents with the contaminated soil can be accomplished with plows, rotary tillers, subsoilers, disc harrows, spike harrows, or spring-tooth harrows. Moisture can be controlled with sprinklers and perforated pipe drains. Tilling, which breaks, mixes, and aerates the soil, tends to increase oxygen content; compaction and flooding tend to decrease oxygen content. Irrigation increases surface moisture; drainage and well points remove excess water from the surface. Various additives are also available for moisture control. For example, synthetic substances that store water can enhance the water retention capacity of the soil; water-repelling agents can accelerate soil drainage and improve water infiltration and percolation.

RESEARCH NEEDS

There has been little operating experience with the use of in-place treatment of contaminated soils. Since the National Contingency Plan requires that any alternative selected for implementation as part of a remedial program must be technically feasible and reliable, research on in-place treatment technologies is critically needed in the following areas to assure that in-place methods can be properly evaluated as potential remedial alternatives.

1) Information on soil processes interfacing with atmospheric processes (i.e., controlling volatilization and photodegradation), including:

   - investigation of photochemical reactions that enhance biodegradation of refractory compounds and those that can produce toxic or undesired breakdown products;
   - laboratory and field-scale analysis of the feasibility of using volatilization/photodegradation as a viable treatment method for volatile/photoreactive hazardous chemicals;

- evaluation of the importance of soil-photochemical reactions to the fate and behavior of photoreactive compounds within the environment;

- refinement of containment/transport models that address volatilization, vapor adsorption, biodegradation, and leaching through the soil matrix; and

- continued development of rapid partition coefficient estimation methods for predicting compound partitioning among air/water/soil systems.

2) Information on chemical reactions relating to the transformation and immobilization of constituents in soil systems, including:

- effects of chemical addition (oxidants, reductants, and polymerizing agents) on the soil properties affecting treatment;

- constituent sorption and precipitation studies at concentrations in the soil matrix characteristic of those found at remedial action sites;

- Eh-pH information for metal species in soils at concentrations representative of remedial action site concentrations; and

- behavior of specific metals, viz., arsenic, beryllium, silver, selenium, mercury, and chromium in soil systems, including the investigation of the reaction of chromium (VI) to chromium (III).

3) Information on biological reactions to stimulate the biodegradation of constituents in soil systems, including:

- potential for combinations of chemical and biological treatment methods for accelerating soil treatment;

- potential for composting of hazardous waste contaminated soil for accelerating biological reactions and for detoxifying and degrading recalcitrant organic constituents;

- evaluation of the biodegradation kinetics and extent of hazardous constituents and metabolites of hazardous constituents sorbed to clay and soil organic matter;

- degradation rates and pathways for chemical classes, including alkyl halides and highly chlorinated organics (PCBs) in the soil treatment zone (upper 5 feet of soil); and

- information concerning the effectiveness of micro-organism seeding compared with no seeding, specifically in terrestrial systems.

4) Information on immobilization reactions in the soil/waste system, including:

- investigation of enhancement of sorption by adding different sorbents, such as activated carbon, straw, synthetic resins. (The specific information needed includes application rates of sorbent in relation to concentrations of contaminant in soil);

- continued development of estimation methods for predicting soil adsorption constants by chemical and physical properties of compounds;

- long-term effectiveness of immobilization of sorbed contaminants on soil; and

- effects of solvents on mobility of organic contaminants in soil systems.

5) Information on leaching in the soil/waste system, including:

   - laboratory experiments to estimate parameters for transport models that can be used to predict behavior under field conditions;
   - field instrumentation to validate transport models under imposed environmental conditions, incorporating the variability under field conditions by designing appropriate sampling stations; and
   - effect of different environmental conditions, including soil moisture, redox potential, and organic content on transport parameters.

SECTION 1
INTRODUCTION

1.1 PURPOSE AND FUNCTION OF THE REPORT

Unplanned and uncontrolled disposal of hazardous wastes frequently results in the contamination of the upper 2 feet of soil. This may severely affect public health, damage terrestrial systems, and destroy or diminish opportunities for land use. Solutions to problems associated with contaminated sites generally follow the procedure specified in the National Contingency Plan (NCP). The NCP process, which is presented in Section 2, is required for sites which receive Federal Superfund money. It also serves as the model for clean-up of non-Superfund sites.

Three types of remedial responses are outlined in the NCP:

- Immediate removal;
- Planned removal; and
- Remedial action.

Immediate removal is employed when there is an "immediate and significant risk of harm to human life or health or to the environment . . ." (40CFR 300.65). Planned removal involves the continuation of immediate response actions, or the implementation of remedial measures at sites not on the National Priorities List. Remedial actions are defined as "responses to realeases on the National Priorities List that are consistent with permanent remedy to prevent or mitigate the migration of a release of hazardous substances into the environment" (40CFR 300.68). The in-place technologies discussed in this report are potentially applicable to each type of response. Selection of in-place treatment as a remedial action response, however, is considered in detail.

The NCP differentiates among initial, source control, and off-site remedial actions. Initial remedial actions are those measures which prevent immediate exposure while long-term solutions are being considered. A security fence and temporary cover are examples of initial remedial actions. Source control remedial actions address realized and potential on-site contamination including, for example, drummed wastes, leaky storage tanks, or contaminated soil. Source control remedial actions contain the hazardous substances where they are located, or eliminate potential contamination by treatment or removal. Off-site remedial actions apply to hazardous substances that have migrated away from the original source of contamination. Off-site measures include provisions for alternative drinking water supplies or treatment of contaminated aquifers. At a given hazardous waste site, any or all of the three types of remedial actions may be applicable.

One of the most common problems found at uncontrolled sites is the contamination of soil and underlying strata. Such contamination arises from leaking drums and tanks, leaking impoundments, direct discharge of wastes in pits, and leaching from solid residues. When large volumes of soil are contaminated and pose a continuing hazard, the development of a remedial action plan will almost certainly require consideration of source control options. In-place treatment is one of a family of source control measures described in the NCP. Others include: no action, excavation and off-site disposal, on-site treatment (e.g., excavation, treatment, and replacement), and physical containment (e.g., cap, hydraulic barrier). In-place treatment can be used to contain the source of contamination (e.g., by immobilization), or to remove it through treatment (e.g., by degradation).

Selection of the appropriate remedial alternative is made through the process outlined in the NCP and is based on site-specific considerations. In some cases, in-place treatment might be considered the most cost-effective option, as indicated by the following scenarios:

- An industrial facility that has produced heavy metal-based chemicals for the past 50 years is closed and the owner wishes to sell the land. Soil analyses, however, indicate that several acres of soil (to a depth of up to 10 feet) at the facility are contaminated with heavy metals on the order of 100 ppm. Excavation of such large quantities of soil would be prohibitively expensive and the benefit relatively low, since the facility is in a highly industrialized area. In addition, it is likely that the new owner would not accept a no-action alternative, and physical containment would interfere with land use. After further investigation, immobilization through in-place treatment is considered the most suitable alternative.

- A farmer decided to supplement his income by disposing of drummed chemical waste in trenches at the edge of his property. A fire in the trenches, however, alerted authorities to his activities. Since the farmer was not able to pay for clean-up, the site was put on the National Priority List making it eligible for Superfund money. Based on the remedial investigation and feasibility study, the U.S. Environmental Protection Agency decided to excavate and remove the drummed wastes and treat the residual contaminated soil in place. An impervious cap was also constructed over the trenches and the site monitored annually.

- A train carrying several tankers of various chemicals derailed in a remote area.,During the accident, a piece of track pierced a tank car carrying benzene, creating two large holes from which the chemical drained. Much of the benzene volatilized immediately. The rest soaked into surface soils. An emergency crew called to the scene estimated that 25,000 gallons of benzene had spilled from the tanker, 10,000 gallons of which remained in the surface soils. Because of the remote location, enhanced microbial degradation was used to remove the benzene from the soil.

The purpose of this report is to provide state-of-the-art information on in-place treatment technologies for contaminated soil. While many of the technologies discussed are applicable for in-place treatment regardless of the depth of contamination, treatment of contamination in the upper 2 feet of soil is emphasized. The report is intended to be used by on-scene coordinators, engineers, regulatory agencies and researchers in evaluating in-place treatment of contaminated surface soils as a remedial alternative.

The report provides a discussion of the major in-place treatment technologies which can be used to treat contaminated surface soil. A methodology for selection of the appropriate technology for a particular site and techniques to modify soil properties are also discussed. The report, however, is not intended to be a guidance manual. Rather, it provides the technical basis necessary to understand the applicability of in-place treatment technologies as a source control remedial measure for contaminated surface soil.

1.2 OVERVIEW

This manual has been organized into two volumes. Volume 1 discusses in-place treatment technologies applicable to contaminated surface soil. Volume 2, available through NTIS, provides background information on the characterization and evaluation of the fundamental processes applicable to site/soil/waste systems.

Volume 1 contains four sections. Section 1 presents the purpose and function of the report and discusses information gaps for in-place treatment. Section 2 gives a general discussion of the various in-place treatment technologies as well as the methodology for selecting the appropriate technology for a particular site. Section 3 presents state-of-the-art information on the technologies. Each technology discussion includes:

- description,
- wastes amenable to treatment,
- status of technology,
- ease of application,
- potential achievable level of treatment,
- reliability of method,
- secondary impacts,
- equipment and exogenous reagents,
- information requirements, and
- sources of information.

A summary matrix with a brief evaluation of each technology is also provided. Section 4 briefly discusses soil modification techniques applicable to several technologies. Soil properties discussed include:

- oxygen content,
- moisture content,
- nutrient content,
- pH, and
- temperature.

The section also contains a table linking soil modification techniques to in-place treatment technologies.

Volume 2 contains three sections and an appendix of chemical data. Section 1 is an introduction. Section 2 provides information on monitoring soil/waste systems. Section 3 addresses fundamental processes in soil/waste systems, including site conditions, physical soil properties, soil sorption, soil microbiology, volatilization and degradation as related to hazardous waste treatment in soil systems. This information is included to provide the user with additional information for making more complex decisions in the analysis of site/soil/waste systems. It is also useful for evaluating the application of additional treatment techniques not specifically discussed in this report. The Appendix provides compound properties and adsorption, degradation and volatilization parameters for various chemicals. These data are important in assessing soil/waste interactions. A glossary is also provided.

SECTION 2

SELECTION OF IN-PLACE TREATMENT TECHNOLOGY

2.1 INTRODUCTION

Selection of appropriate remedial action technologies follows the procedure specified in the National Contingency Plan (NCP). This procedure is outlined in Figure 2-1. First, a preliminary assessment, called scoping, is conducted to determine the type of response expected (initial, source control, or off-site remedial action). Scoping relies on available information and provides the basis for funding requests. This is followed by a remedial investigation to determine "the nature and extent of the problem presented by the releases. This includes sampling and monitoring, as necessary, and includes the gathering of sufficient information to determine the necessity for and the proposed extent of remedial action." (40 CFR 300.68 (f)). The remedial investigation also re-evaluates the conclusions of the scoping phase. Alternative remedial technologies are then suggested and screened according to the factors given in the figure. Finally, the most promising technologies are analyzed in detail and the most cost-effective alternative selected.

Evaluation of in-place treatment technologies is a part of this overall process. The specific methodology for selecting an in-place treatment technology (beginning with the remedial investigation) is depicted in Figure 2-2. It is assumed here that the results of scoping indicate source control remedial action to be appropriate. It is also assumed that contaminated surface soils are involved, so that the technologies in this report are potentially applicable.

This Section begins with a general discussion of in-place treatment technologies, followed by four sections that parallel the procedure outlined in Figure 2-2. The development of alternatives in selecting in-place treatment type and the detailed analysis to select appropriate in-place treatment technologies are emphasized. Finally, consideration is given to information gaps and the need for further research pertaining to in-place treatment as a remedial action alternative.

2.2 DISCUSSION OF IN-PLACE TREATMENT TECHNOLOGIES

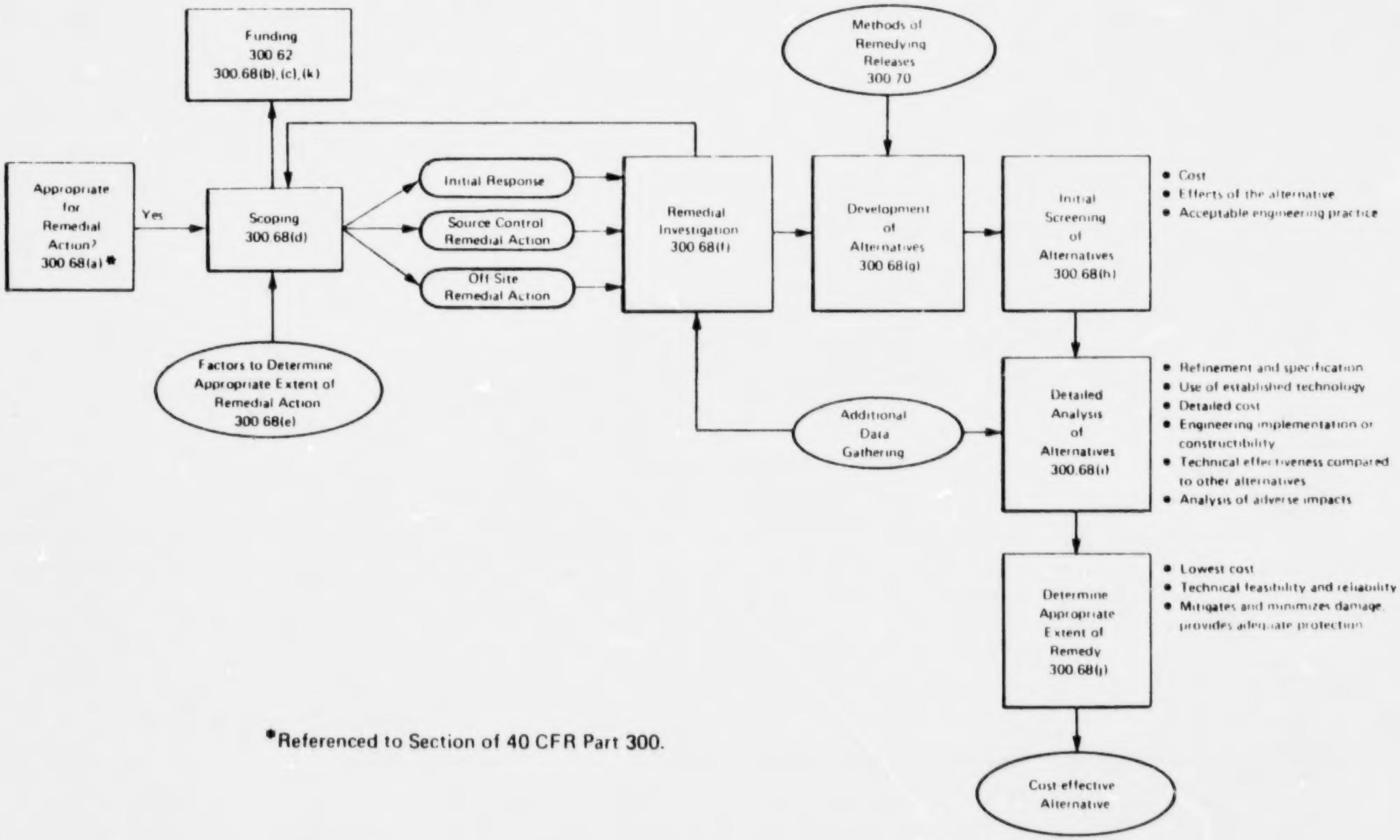
There are five major categories of in-place treatment technologies that can be defined in terms of their primary action on the contaminants contained within the soil:

1. extraction,
2. immobilization,
3. degradation,
4. attenuation,
5. reduction of volatilization.

2.2.1 Extraction Techniques

Extraction techniques actually remove the undesired contaminant from the soil by dissolution in a fluid which is subsequently recovered and treated either on site or at another location. This technique offers a more or less permanent solution to the problems pre-existing at the remedial action site. The problem of ultimate disposal of the contaminants

Figure 2-1. Detailed sequence – phase VI – remedial action (40 CFR, part 300.68)


Appropriate for Remedial Action? 300.68(a)*
Yes
Funding 300.62 300.68(b), (c), (k)
Scoping 300.68(d)
Factors to Determine Appropriate Extent of Remedial Action 300.68(e)
Initial Response
Source Control Remedial Action
Off Site Remedial Action
Remedial Investigation 300.68(f)
Methods of Remedying Releases 300.70
Development of Alternatives 300.68(g)
Additional Data Gathering
Initial Screening of Alternatives 300.68(h)
• Cost
• Effects of the alternative
• Acceptable engineering practice
Detailed Analysis of Alternatives 300.68(i)
• Refinement and specification
• Use of established technology
• Detailed cost
• Engineering implementation or constructibility
• Technical effectiveness compared to other alternatives
• Analysis of adverse impacts
Determine Appropriate Extent of Remedy 300.68(j)
• Lowest cost
• Technical feasibility and reliability
• Mitigates and minimizes damage, provides adequate protection
Cost effective Alternative

*Referenced to Section of 40 CFR Part 300.

Source: Ehrenfeld and Bass, 1983.

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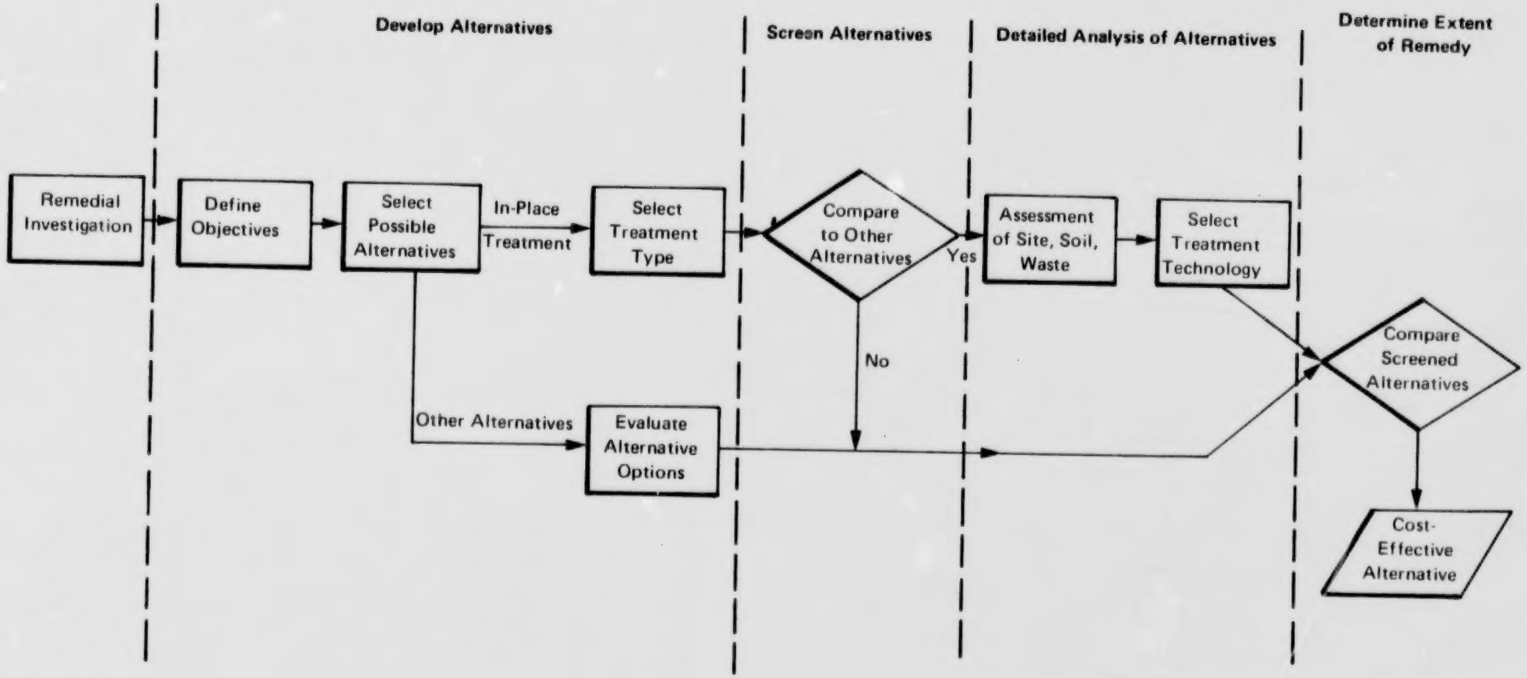
Figure 2-2. Methodology for selecting in-place treatment technology.


Develop Alternatives
Screen Alternatives
Detailed Analysis of Alternatives
Determine Extent of Remedy
Remedial Investigation
Define Objectives
Select Possible Alternatives
In-Place Treatment
Select Treatment Type
Compare to Other Alternatives
Yes
Assessment of Site, Soil, Waste
Select Treatment Technology
No
Other Alternatives
Evaluate Alternative Options
Compare Screened Alternatives
Cost-Effective Alternative

is, however, moved to another location and another set of processes. The ultimate treatment and disposal of the contaminated extraction fluid can often be carried out under more favorable technical conditions, at significantly lower risk, and at reduced costs compared to other in-place treatment options.

2.2.2 Immobilization Techniques

Immobilization techniques are designed to capture the species within the contaminated soil mass. Immobilization reduces the tendency of the contaminant to enter the groundwater, surface water, or atmospheric exposure pathways. The immobilized contaminants, however, remain in the soil, leaving open the possibility for exposure via direct contact or contaminant migration under changed conditions in the future.

The three major classes of immobilization techniques are: adsorption (sorption), ion exchange, and precipitation.

Adsorption includes techniques designed to capture the contaminants on the soil particles by adjusting the properties within the soil system. In addition, adsorptive materials, such as activated carbon can be admixed into the soil to enhance its inherent adsorptive properties. Adsorption can be applied to both inorganic and organic contaminants.

Ion exchange is a means for immobilizing inorganic species similar in nature to physical adsorption. Initially mobile metal ions exchange positions with innocuous cations and become bound to clay particles in the soil system. Many heavy metal contaminants that pose significant risks are quite tightly bound by common clay minerals. The activity of natural ion exchange in soils can be enhanced by admixing synthetic ion exchange resins. Such resins can be tailored to be highly selective for particular metals. Ion exchange techniques are applicable only to inorganic contaminants.

The final immobilization technique is precipitation. Inorganic contaminants that are initially soluble are caused to react and form compounds of very low solubility. The insoluble products are thereby retained by the soil system within the initially contaminated region instead of being removed by infiltration and groundwater flow. The precipitating agent can be added directly, for example, in the form of sodium sulfide (Na_2S), or it can be generated in-place by a chemical or biochemical reaction.

2.2.3 Degradation Techniques

The third category of treatment technologies is degradation. This is a family of methods which converts the contaminant species into an innocuous or less toxic compound or compounds. In general, degradation is applicable to organic compounds. There are a number of limited cases in which degradation is applicable to inorganic species. Highly toxic hexavalent chromium, for example, can be reduced to the less toxic trivalent form by the addition of reducing agents. Degradation is often used in combination with immobilization for inorganic contaminants. Following the above example, trivalent chromium can be readily precipitated in the hydroxide form. By and large, however, the degradation techniques are of broader applicability to organic contaminants than to inorganic.

Chemical degradation techniques convert contaminant species by promoting the natural capacity of the soil to support oxidation or reduction reactions or by adding suitable reagents. Reactive organic compounds, such as vinyl monomers, may be polymerized in-place by the addition of catalysts to form immobile species.

Biological techniques utilize the action of micro-organisms to break down organic compounds into innocuous or less toxic metabolic products. The naturally occurring micro-organisms found in nearly every soil system can often be used to degrade organic contaminants. The soil system may have to be modified to promote the activity of naturally found organisms. Promotion includes addition of nutrients and aeration of the soil. If the intrinsic micro-organism flora do not work on some set of contaminants, selectively adapted innoculants or even perhaps genetically engineered species, can be added to the soil mass.

The last degradation technique involves photodegradation (photolysis). The action of the ultraviolet portion of sunlight can result in the breakdown of many complex and toxic organic compounds. Organic species brought to the surface by volatilization or mechanical mixing may be broken down by sunlight incident on the surface. The compounds must move toward the surface in order for this technique to be practical.

2.2.4 Attenuation

Attenuation, the fourth category of in-place treatment techniques, involves admixing clean soils or other bulking agents to reduce contamination to an acceptable level. This approach has been used to reduce the hazards due to ingestion or direct contact.

2.2.5 Reduction of Volatilization

Finally, reduction of volatilization, the last major category of treatment techniques, is applicable to exposure via the air pathway. Volatile organic contaminants pose a significant risk via this pathway. Techniques for reducing volatility include those which impede the diffusion of volatile contaminants and others which reduce the inherent tendency for volatilization to take place. Flow toward the surface can be inhibited by reducing the soil vapor pore volume. Alternatively, the volatility of the contaminant materials can be reduced by techniques such as cooling the soil to lower the vapor pressure.

2.3 DEVELOPMENT OF ALTERNATIVES

The first phase in selecting the appropriate in-place treatment technology, as shown in Figure 2-2, is the development of alternatives. This takes place after scoping and the remedial investigation have been completed. This means that the type of remedial response has been determined. For this discussion, it is assumed that source control remedial actions are appropriate, and that information from the remedial investigation is available to determine the nature and extent of the contamination problem. Such information would include:

- type of waste present (organic, inorganic, chemical components),
- estimate of waste quantity,
- waste form (free liquid, solid, contaminated soil),
- waste location (areal extent, depth, relationship to water table),
- exposure pathways (groundwater, surface water, air, direct contact),
- population threatened (human, environmental).

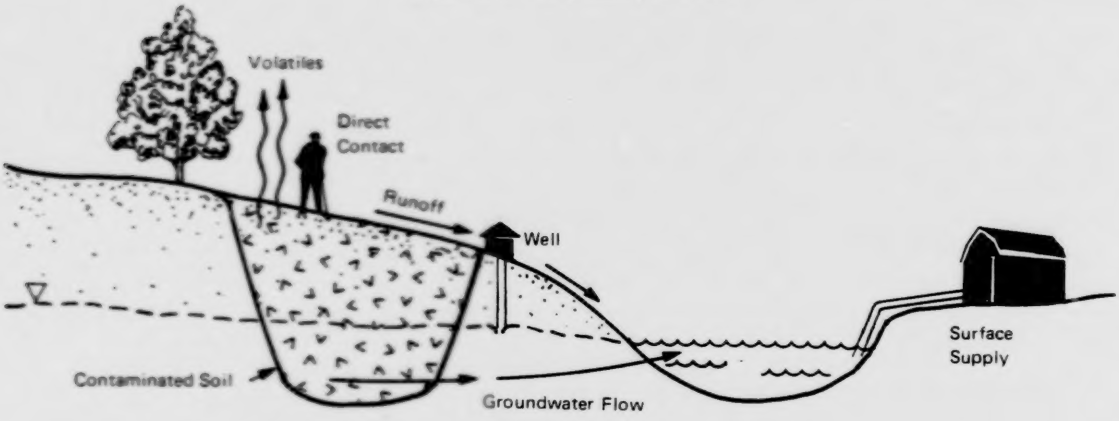
The remedial investigation provides the basis for the selection processes through the comparison and screening of initial remedial alternatives.

2.3.1 Definition of Objectives

The first step in developing alternatives is to define the objective of the remedial program. This step, which is not explicitly specified in the NCP, is iterative and occurs throughout the selection process. The objectives are refined and modified as new information is obtained. It is necessary, however, to have a clear understanding of the remedial objectives before considering alternative remedial actions, since selection depends on the desired result.

An objective can be defined as an aim or goal of the remedial program. Based on current legislation, the primary objective for remedial action at Superfund sites is to reduce risk to an acceptable level, while minimizing cost. The purpose of the selection process, therefore, is to determine which alternative is most "cost-effective" (defined in 40 CFR 300.68(j) as "the lowest cost alternative that is technologically feasible and reliable and which effectively mitigates and minimizes damage to and provides adequate protection of public health, welfare, or the environment"). Secondary objectives can be used to further define the primary objective. They may consider a particular exposure pathway or address other technical requirements, local regulations, or political concerns. Together, the objectives specify the end-result or outcome desired to be achieved through implementing the selected remedial action technologies.

Figure 2-3. **Exposure pathways.**



Source: Arthur D. Little, Inc.

Figure 2-3 depicts a generalized site containing a large quantity of contaminated soil. The remedial objective at the site might be to reduce risk (a function of the contamination, the pathways and the receptors) by minimizing exposure along each of the pathways depicted (direct contact, air, groundwater, surface water). Alternatively, if there was no drinking water use downgradient or downstream of the site, the objectives might be to minimize exposure along the air and direct contact pathways.

2.3.2 Selection of Possible Alternatives

Once objectives have been determined, it is necessary to select alternatives that would meet the objectives from the many available source control remedial action technologies. For the example in Figure 2-3, a security fence, cap and slurry wall combination, removal and off-site disposal, on-site treatment, and in-place treatment would all potentially reduce exposure along each of the pathways. They, therefore, can be considered in the initial development of alternatives, along with any other technology or combination of technologies which have a similar effect. The purpose of the initial selection of possible alternatives is to consider as many technologies as possible so that the cost-effective alternative is not overlooked. Subsequent screening and detailed analysis of alternatives serve to single out those technologies that are most cost-effective in meeting the objectives.

The remainder of this Section emphasizes the considerations particular to selecting in-place treatment technologies. The evaluation of other technologies follows a similar path which is not discussed, except where the two paths converge.

2.3.3 Selection of an In-place Treatment Type

The selection process described herein fits into the two-step procedure commonly used in remedial investigation/feasibility studies (RI/FS). It begins with a preliminary evaluation of all the potential in-place treatment methods available and the identification of all those that are potentially applicable to the site, and that are consistent with the objectives. A very rough screen can be made on the basis of the exposure pathways and the chemical nature of the contaminants. Table 2-1 shows a general applicability matrix. Reference to this table permits selection of the family of techniques applicable to any combination of pathway and compound. For example, if the objectives contain a requirement to reduce the risk from organic compounds via direct contact, then extraction or any of the degradation techniques would be potentially applicable. None of the immobilization techniques would be useful. On the other hand, if the objective were to reduce the risk from inorganic species via groundwater, then removal and immobilization via adsorption, ion exchange, or precipitation would be potentially applicable. Degradation would have limited applicability, depending on the specific inorganic species.

TABLE 2-1. GENERAL APPLICABILITY MATRIX

Technology	Air	Groundwater	Surface Water	Direct Contact	Inorganic	Organic
EXTRACTION	X	X	X	X	X	X
IMMOBILIZATION						
Adsorption	–	X	X	–	X	X
Ion exchange	–	X	X	–	X	L
Precipitation	–	X	X	–	X	–
DEGRADATION						
Chemical	X	X	X	X	L	X
Biological	X	X	X	X	L	X
Photolysis	X	X	X	X	–	X
ATTENUATION	L	–	–	X	X	X
VOLATILE REDUCTION	X	–	–	–	L	X

X = Potentially Applicable
– = Not Applicable
L = Limited Applications

If multiple pathways are involved, as is very often the case, technologies potentially applicable to all pathways should be considered. For example, dioxin-contaminated soils may pose a risk through both ingestion of surface soils and groundwater contamination. Although immobilization techniques via adsorption would be potentially applicable for groundwater, as shown in Table 2-1, the inapplicability of this approach when direct contact is included would rule it out, or it would at least require adsorption to be used in combination with another technology.

The preliminary screening procedure should be broadly construed. If there is any question, a general class of in-place treatment should be left in the portfolio of options to be evaluated in the detailed steps further along the process. Combinations of techniques should also be included in the first round.

The list of potentially applicable alternatives can also be narrowed down by consideration of the time available for treatment, or by the rough reduction levels if available at this stage of the analysis. Some of the processes take a very long time (e.g., photodegradation) and may be inappropriate at a site requiring clean-up over a limited time period.

Using only information available from the initial remedial investigation, one may find it possible to eliminate some of the technologies, or at least note that the likelihood of their feasibility is lower than that of other options. Immobilization techniques depend perhaps more than any other option on the intrinsic properties of the soil system. Adsorption can be expected to be fairly high in soil systems containing high clay and organic content. Waste sites where soils are predominantly sandy in nature would probably be poor candidates for techniques based on adsorption, although additives could be used to enhance the poor intrinsic soil properties.

The effectiveness of any one technique or combination of techniques depends on many site-specific and waste-specific factors. The procedure for introducing these factors into the evaluation and final selection of the single or small family of cost-effective techniques is developed in the following sections of this document.

2.4 SCREENING OF ALTERNATIVES

Once a list of alternative technologies and technology combinations has been developed, it then becomes necessary to narrow the list for further detailed analysis. The three criteria used for this screening are:

- costs,
- effects of the alternative, and
- acceptable engineering practice.

Costs include capital, operating, and maintenance costs. Technologies that are significantly more expensive than other alternatives without providing a greater degree of benefit or reliability can be excluded from further consideration. For example, if removal by extraction costs X dollars and removal by excavation costs 10X, excavation would no longer be considered, assuming that extraction would meet the second and third criteria.

Evaluating the effects of the alternative involves two considerations:

(1) whether implementing the alternative causes adverse environmental effects. Some biodegradation techniques, for example, produce toxic metabolic products which bio accumulate in the course of detoxifying the target contaminant(s); and

(2) whether the technology has sufficient capabilities relative to the objectives and associated performance requirements. In other words, can the technology achieve the required level of source control?

If either consideration produces an unsatisfactory finding, the technology option would not be considered further.

Acceptable engineering practice means that the alternative is feasible, given site-specific conditions, and is considered an applicable and reliable means of addressing the problem.

These screening criteria are evaluated based on available information according to the judgment of the lead agency or other decision-makers. The screening should result in a shorter list of technologies to be evaluated in detail.

2.5 DETAILED ANALYSIS OF ALTERNATIVES

The detailed analysis of alternatives involves further investigation in five areas (40 CFR 300.68(i)(2)):

1) refinement and specification of alternatives in detail;

2) detailed cost estimation, including distribution of costs over time;

3) evaluation in terms of engineering implementation or constructability;

4) an assessment of how well the alternative meets the remedial objectives; and

5) an analysis of any adverse environmental impacts, methods for mitigating these impacts, and costs of mitigation.

For in-place treatment technologies these steps involve (1) assessment of waste, soil, and site-specific variables, and (2) selection (including detailed specification) of an in-place treatment technology within the treatment category.

2.5.1 Assessment of Waste, Soil and Site-specific Variables

Many waste, soil, and site-speific variables affect the technical feasibility and effectiveness of in-place treatment. Some of these variables can be conveniently established as part of the remedial investigation. Others may require independent bench-scale or pilot studies directly related to treatability. Each of the important variables is discussed below under the following sub-headings:

- waste characteristics,
- site characteristics, and
- waste/soil system characteristics.

These discussions are followed by a discussion of laboratory and pilot-scale testing.

2.5.1.1 Waste Characteristics

Soil core and soil pore water samples should be obtained and analyzed to determine the chemical contaminants present, the areal extent and depth of contamination, and the range of contaminant concentrations at presumed source locations and along expected pathways of migration.

Soil and groundwater samples from contaminated areas and control (background) areas should be analyzed for:

- Elemental and Inorganic Constituents:
  - — Metals and metalloids (As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn),
  - — Total organic carbon (TOC),
  - — Total Kjeldahl nitrogen (TKN),
  - — Sulfate
  - — Chloride.
- Organic Constituents:
  - — Priority pollutants (volatiles, acid extractables, and base/neutrals),
  - — Others known or expected to be present, based on past activities at the site.

Based on the analytical results, a list of contaminants within each group that are present at levels in excess of background should be compiled. Maps should be prepared showing contaminant locations and concentrations.

To assist in evaluating pathways of migration, and in designing in-place treatment processes, the following physical/chemical properties should be derived from the literature or estimated for each of the identified waste constituents:

- solubility in water (and in other solvents, if flushing is an alternative of interest);
- vapor pressure;
- soil/water partition coefficient, K_{oc}, for organic waste constituents (K_{oc} is defined as the Freundlich adsorption coefficient (K) divided by the weight fraction organic carbon (f_{oc}) in the soil, i.e., $K_{oc} = K/f_{oc}$);

- Henry's Law Constant (used in evaluating the partitioning of a contaminant between soil pore water and the vapor phase); this may be derived from the vapor pressure/water solubility ratio for chemicals of limited water solubility (<1m);

- standard electrode potential (used in evaluating oxidation/reduction alternatives).

2.5.1.2 Site Characteristics

Significant site variables are ones that affect pathways of migration of waste constituents, and/or design and implementation of in-place treatment processes. Site characteristics that are important in the selection of in-place treatment methodology include:

- Location — While the significant characteristics of a given site are usually unique, useful hypotheses about pathways of migration and estimates of parameters needed to calculate migration rate can often be developed from available regional data, and keyed to location, topography, surface drainage patterns, flood potential, subsurface stratigraphy, groundwater flow patterns, and climate.

- Topography — Topographic variables are important in evaluating surface drainage, runon and runoff potential to and from contaminated areas of the site, and logistics of moving and/or placing equipment for in-place treatment.

- Stratigraphy — The nature of subsurface soils, determined by examination of soil core borings to bedrock, is an important input to evaluation of pathways of migration in both the unsaturated and saturated zones.

- Groundwater Levels (Equipotential Surfaces) — Seasonal maps of water table contours and piezometric surfaces, developed by analysis of groundwater monitoring well data, are important in predicting groundwater flow directions and hydraulic gradients.

- Groundwater Flow — Information on permeability and porosity of subsurface strata, combined with data on hydraulic gradients, is important in predicting groundwater flow velocities and in estimating contaminant transport times.

- Meteorology and Climate

  — Wind velocity and direction is important in determining the potential for migration of airborne particulate matter and volatile waste constituents.

  — Temperature, including seasonal or monthly means and duration of the frost-free period, is important in estimating rates of biological and chemical reactions in-place, and in evaluating the technical feasibility of in-place methods. If possible, data on soil temperatures as well as ambient temperatures should be obtained, since they often differ.

  — Precipitation, including annual, seasonal or monthly rain and snowfall, is an important parameter in determining a water balance for the site, and in evaluating leachate potential.

  — Evapotranspiration is also important in developing a water balance for the site. It is often estimated from temperature and the nature of vegetative growth at the site.

- Soil Properties
  - pH is an important variable in evaluating mobility of many metal contaminants, as well as organic acids and bases, and in designing several of the in-place processes discussed in this report.
  - Cation exchange capacity (CEC) is an important determinant of the mobility of metallic species in soils; if the CEC is sufficiently high to adequately immobilize the heavy metals present in the soil, no further action may be necessary; if one remedial objective is to reduce heavy metal migration from expected "no action" levels, a potential in-place treatment method might involve increasing the intrinsic CEC of the soil.
  - Redox potential (Eh) is important in determining the stability of various metallic and organic species in the subsurface environment of the site, and it also might be modified by in-place treatment.
  - Organic carbon content is a major variable affecting adsorption, and hence mobility, of organic species in the subsurface environment.
  - Microbial content as a function of depth is an important variable, if potentially biodegradable constituents are present in the waste.
  - Soil type (e.g., clay, till, sand, fractured bedrock) is a major variable affecting rates and routes of groundwater migration and contaminant transport.
  - Hydraulic conductivity is important in determining feasibility and spacing of drains and wells.
- Trafficability — Factors that affect the mobility and/or placement of equipment on the site, and the ability to perform tillage and other in-place treatment operations need to be considered in the remedial action design. Significant variables include: bearing capacity, traction capacity, soil strength, slipperiness, stickiness, moisture content, clay content, presence of debris, structures and/or vegetation, and slope of the terrain (topography), as mentioned earlier.
- Potentially Exposed Human Populations and Sensitive Ecological Environments
  - Groundwater and surface water usage, especially downgradient of the site, are important in evaluating risks and environmental benefits of remedial alternatives.
  - Size of population and nature of ecological resources downgradient and downwind of the site are also important variables for risk assessment.

2.5.1.3 Waste/Soil System Characteristics

Design and implementation of an in-place treatment process requires information on characteristics of the waste/soil system as a whole. The important variables are:

- Depth of Contamination — If contamination is limited to the upper 6-8 inches of the soil and it is well above the water table, in-place treatment techniques may be much more easily applied than if the contamination extends well below the plow layer and into the seasonally high water table.
- Contaminant Concentrations and Quantities — The efficiency and effectiveness of many in-place processes depend upon both contaminant concentration levels and the total quantity of each contaminant present in a given area.

- Treatability — Based on the various waste, soil, and system characteristics discussed above, an analysis can be made of routes and rates of contaminant migration and the potential for damage to human health and the environment as a function of time under conditions of no action. The in-place methods discussed in this report are intended for consideration in situations in which naturally occurring immobilization, degradation, attentuation, and volatilization processes are insufficient in and of themselves to meet defined objectives within an acceptable time frame. For practical purposes, therefore, in-place treatment will require physical modification of the waste/soil system and/or addition of exogenous agents to accelerate the rate of naturally occurring remediation processes or to induce processes in-place to meet the remedial objectives.

The in-place methods discussed in this report are basically intended to alter the waste, soil, and/or waste/soil system characteristics determined to exist at the site prior to treatment. Any one of the generic methods under consideration, however, needs to be specifically adapted to each particular site contamination situation in order to achieve desired system characteristics after treatment. Table 2-2 summarizes the treatment variables that need to be determined to assess the capability of in-place treatment alternatives to achieve remedial objectives.

Waste and soil characteristics are useful in prescreening in-place alternatives for potential applicability in meeting remedial objectives. However, the present state of the art of in-place treatment is not sufficiently advanced to have a comprehensive data base, or to allow calculation of optimum conditions for degradation, detoxification, and/or immobilization of waste constituents. For those alternatives identified as potentially applicable, bench scale treatability studies will generally be necessary to assess technical feasibility further and to establish design parameters for implementation and costing. The combined use of waste, soil and system characteristics in the assessment of several generic in-place alternatives is illustrated below.

- No Action Alternative

In situations where the intrinsic properties of the soil are adequate to block migration of waste constituents along pathways of concern, the no action alternative is likely to be the most cost-effective. In all cases, the inherent assimilative capacity of the soil for the waste constituents of concern should be evaluated (see Overcash and Pal, 1979 and USEPA, 1983).

Even if naturally occurring degradation, immobilization, and attentuation processes are deemed inadequate to meet remedial objectives, assessment of these processes provides a useful baseline for designing additional in-place remedial measures. For example, soil systems containing high clay and organic content may adequately immobilize both heavy metal and organic chemical constituents of waste by natural adsorption processes, provided that the assimilation capacity of adsorption sites is not exceeded. Waste sites where soils are predominantly sandy would have little potential for immobilizing waste constituents. No action might be appropriate for the clay soils, but not for the sandy soils. For two equally contaminated sites of the same size, less additional adsorbent might be required to immobilize constituents in the clay soil where its natural assimilative capacity has been exceeded than in the sandy soil.

- Extraction Alternative

Flushing or "solution mining" of contaminants requires identification and bench-scale testing of potentially suitable solvents and the design of a recharge/discharge system to effect flushing in the field.

- Immobilization Alternative

Immobilization processes are designed essentially to reduce leaching (or volatilization) of hazardous waste constituents to acceptable levels. Depending upon the particular waste/soil system, immobilization may be accomplished through physical or chemical adsorption, ion exchange, or precipitation. In general, immobilization of contaminants at uncontrolled hazardous waste sites requires the incorporation of physical or chemical adsorbents into

TABLE 2-2. TREATMENT VARIABLES FOR IN-PLACE TREATMENT TECHNOLOGIES

Technology	Treatment Variables	Comments
EXTRACTION	• Solubility of waste constituents in solvent • Concentrations of waste constituents • Rate of dissolution of adsorbed species	Solubilities of constituents vary with different solvents.
IMMOBILIZATION		
Sorption	• Adsorptive capacity of sorbent for specific waste constituents • Concentrations of sorbates, including naturally occurring substances • Soil pH • Soil moisture • Soil/water partition coefficient (K_{oc})	All sorbates compete for adsorptive capacity of sorbent.
Ion Exchange	• Cation (or anion) exchange capacity of clay, resins, or zeolites • Concentration of ions in soil water • Soil pH	Clays and zeolites are used to treat cations (metal ions), resins for both cations and anions.
Precipitation	• Concentration of soluble metals • Stability of precipitate relative to dissolved species • Soil pH • Oxidation state of metal ions • Soil oxygen content • Reactivity of precipitate	Sulfides may transform to more soluble sulfates under long periods of aerobic soil conditions
DEGRADATION		
Chemical	• Redox potential of waste/soil system • Soil oxygen content • Presence of catalyst(s) • Polymerization potential of wastes • Soil pH • Soil moisture • Soil temperature	Oxidation/reduction products may be more mobile and/or more toxic than the parent compound; chemical oxidants are non-selective and may preferentially oxidize organic matter in soils.

(continued)

TABLE 2-2 (Continued)

Technology	**Treatment Variables**	**Comments**
Biological	• Biodegradability of waste constituents (half-life) • Soil pH • Micro-organisms present (type; population) • Soil oxygen content • Soil moisture • Soil nutrient content (C:N:P ratio) • Soil temperature • Rates of biodegradation, or rates of leaching	Caution is needed to ensure that contaminants are not toxic to micro-organisms. Chemical-specific micro-organisms may be encouraged by manipulating treatment variables.
Photolysis	• Absorption spectra of waste constituents (> 290-nm wavelength range) • Half-life of photolysis; photolysis products • Volatility of waste constituents (vapor pressure, Henry's Law Constant)	Photolysis products may be more toxic than parent compound.
ATTENUATION	• Site-soil assimilative capacity • Feasibility of mixing uncontaminated material with contaminated soils	Assimilative capacities are available for many heavy metals, but not for organics.
REDUCTION OF VOLATILIZATION	• Volatility of waste constituents and dependence on temperature (vapor pressure, Henry's Law Constant) • Soil moisture • Soil temperature	

Source: Arthur D. Little, Inc.

the contaminated soil, or the addition of ion exchange or precipitating agents. Optimum additive concentrations are best determined using laboratory treatability studies with the waste/soil system. Optimum conditions for in-place immobilization can be selected by varying the treatment parameters and determining the minimum rate of leaching of the constituents of concern. The minimum achievable leaching rate should then be compared with the desired rate to meet remedial objectives.

- Degradation Alternative

Management of the soil/site system to increase the rate of biodegradation is a potential option to be considered for sites contaminated with organic chemical wastes. As discussed above, part of the site characterization will involve a determination of the presence or absence of micro-organisms (e.g., aerobic bacteria, anaerobic bacteria, actinomycetes, fungi, and algae) for representative areas of contamination. Part of the waste characterization will involve analyses to determine the carbon:nitrogen:phosphorus ratio. If the C:N:P ratio is not optimal for micro-organism growth, bench-scale experiments should be conducted to determine whether adjustment of this ratio will increase the concentration of micro-organisms in the soil and the rate of biodegradation. These initial experiments should be done with samples of contaminated soils from the site at dissolved oxygen concentration levels characteristic of the respective contaminated areas if possible.

Experiments should also be done to determine the effect of various oxygen levels on soil micro-organism count and rate of biodegradation. If nutrient and oxygen adjustments are insufficient to stimulate the growth of micro-organisms or to increase the biodegradation rate adequately, experiments might be performed to innoculate the soil/waste mixture with activated sludge, commercially developed micro-organisms likely to feed on the particular contaminants in the soil, or soil from the site or control area that has a high micro-organism count. Rates of biodegradation should be measured systematically as a function of nutrient concentrations, oxygen, and micro-organisms to establish optimum conditions for degradation.

Once these conditions have been determined, an in-place method capable of achieving these conditions in the field would have to be designed. There are a number of possibilities. For contaminated areas within 2 feet of the surface, simple tilling of the surface soils may introduce sufficient oxygen into the system to accelerate the rate of biodegradation. Depending upon the laboratory results, it may also be necessary to innoculate the surface with additional micro-organisms, adjust the pH and nutrients, and/or adjust the moisture content. For contaminated areas at greater depths, oxygen nutrient and possibly micro-organism additions will almost certainly be required to achieve satisfactory degradation rates. Conceivably, deeper constituents could be flushed out of the soil and reapplied in a controlled manner to the soil surface for biological treatment as described above for surface contaminants.

In areas where contaminant concentrations are so high as to be toxic to micro-organisms, the contaminated soil might be mixed with uncontaminated soil to reduce overall concentrations to levels that could then be successfully biodegraded in-place.

In the soil/waste system, biodegradation under the optimum conditions established in the laboratory experiments will generally compete with leaching, or volatilization of the waste constituents or their intermediate degradation products. Laboratory experiments should be performed to compare degradation rates with leaching and volatilization rates. If leaching or volatilization is rapid compared to biodegradation, it may be necessary to modify soil properties for some distance along the pathways of migration to immobilize the biodegradable constituents.

The laboratory experiments performed to establish the optimum achievable rate of degradation should determine not only the rate of disappearance of the parent compound, but also the chemical identity and rate of disappearance of the degradation products over time. The toxicity of partially degraded fractions should be determined either from the literature or via a bioassay. If the biodegradation products are toxic and do not degrade, then biodegradation would generally have to be considered infeasible.

Depending upon the nature of the contaminants present and the treatment objectives, chemical reagents may also have to be incorporated into contaminated surface soils, or injected into deeper contaminated layers, to bring about detoxification or degradation reactions. Such reactions might involve oxidation, reduction, or polymerization, for example. Appropriate reagents, reaction rates, and the leachability and toxicity of reaction products will generally have to be determined by laboratory treatability studies.

- Attenuation Alternative

Federal and State guidelines for land application of sewage sludges specify acceptable levels of heavy metal accumulation in soils (mg/kg). If these or other specified levels are exceeded at a site, they can be attenuated to acceptable levels by mixing with clean soil. The amount of soil required is determined by the metal that must be attenuated to the greatest extent to meet standards. Attenuation is also applicable, in principle, to organic contaminants. In practice, assimilative capacities of soils, which must be known to design attenuation systems, have only been established for heavy metals.

- Reduction of Volatiles

Suppression of vapor transport from contaminated soils may be desirable if contaminants or their degradation products can escape from the untreated soils at levels and rates potentially damaging to target organisms. Simple models are available to estimate the loss and transport of volatiles from soil systems. These models generally require data or estimates of the vapor pressure and solubility of the contaminants, as well as knowledge of the meteorological conditions at the site. Effectiveness of methods to reduce volatiles should be tested in the laboratory to establish design parameters for a field system (Farmer et al., 1980).

2.5.1.4 Laboratory and Pilot-scale Testing

Laboratory (bench-scale) and pilot-scale testing may be required to evaluate the technical and practical feasibility of in-place treatment methods for contaminated soil prior to full-scale implementation. Testing may be used to establish the following at in-place treatment sites:

1) The critical soil level for the waste at which treatment (degradation, detoxification, and/or immobilization) is ineffective due to toxicity or mass flow conditions.

2) The rate of degradation or detoxification of organic constituents, i.e., the half-life, and the extent of immobilization of inorganic constituents.

3) The mobility, toxicity, and biodegradability of partially degraded waste constituents or waste fractions.

4) Criteria for management of the soil and site to enhance the natural ability of the soil to attenuate constituents by determining optimum conditions for degradation, detoxification, and/or immobilization.

5) Parameters and constituents that should be monitored to indicate contaminant migration to receiver systems including groundwater, surface water, and atmosphere.

6) Technical feasibility and potential costs associated with using techniques based on management of the site/soil assimulative capacity for accomplishing the treatment required for a particular site/soil/waste system.

In principle, the direct costs for labor and equipment for laboratory or pilot-scale testing, as well as the indirect costs of delaying implementation until test results are obtained, will be determined by the complexity of the experimental design. That will depend, in turn, on the number of experimental variables to be controlled and/or monitored, the types of equipment required, the length of time and number of samples required to obtain the desired information with the requisite precision, or reliability, and prior operating experience with the process. Each of these factors will be specific to the process under study and thus cannot be specified *a priori*.

Certain elements of the testing program, however, are likely to be common to most other laboratory and pilot-scale testing programs. Among those elements are statistical sampling requirements, sampling equipment, sample collection, preservation, shipping and storage, and chemical analysis. Basic considerations and reference sources for each of these areas are described briefly under the respective headings below.

2.5.1.4.1 Statistical Sampling Requirements

The purpose of sampling is to permit estimation of the properties of interest in a cost- and time-effective manner. The sampling program chosen to achieve this objective will depend on the precision required of the estimation. Sampling plans commonly used for soil testing programs include simple random sampling, stratified random sampling, and systematic sampling. Statistical considerations associated with these and other types of sampling plans are discussed in detail in Black, 1965; Walsh and Beaton, 1973; and "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," 1980.

2.5.1.4.2 Sampling Equipment

The sampling equipment used to obtain samples for subsequent testing depends on the type of sample required and on the soil type and depth from which the sample is to be obtained. The materials from which the sampling equipment is constructed must be chosen so that those surfaces in direct contact with the soil will not contaminate the sample with any species which may interfere in the chemical analysis. General descriptions of the types of equipment which may be used for soil sampling with directions for their use are in Soil Conservation Service, 1972; and U.S. EPA, 1982.

2.5.1.4.3 Sample Collection, Preservation, Shipping and Storage

Procedures used for sample-handling and storage will depend on the characteristics to be determined. In the simplest case, the sample may be air-dried under ambient conditions and subsequently stored in clean containers until analyses are performed. However, special precautions may be required in cases where the characteristic to be determined may be affected by the conditions of handling, shipping, and storage. Those precautions may include addition of chemicals to fix or retard changes in the concentration of the species of interest, freezing the sample, or performing the analysis at the time of collection. Guidelines for sampling handling and storage are provided in U.S. EPA, 1982; and American Public Health Association, 1975.

2.5.1.4.4 Chemical Analysis

Methods applicable to the determination of a wide variety of organic and inorganic compounds, elements, anions, and physical and chemical properties are readily available in the technical literature. Representative sources include: Walsh and Beaton, 1973; U.S. EPA, 1982; American Public Health Association, 1975; David, 1978; and Purdue University, 1977.

2.5.1.4.5 Monitoring

In general, laboratory and pilot-scale testing do not simulate field conditions exactly. Therefore, the effectiveness of the treatment process selected must be monitored after implementation. Soil core and soil pore water in the treatment zone and along pathways of migration must be sampled and analyzed to determine whether the treatment process is functioning according to design. Appropriate parameters to monitor would generally be selected from among the waste constituents expected to be treated, and the degradation products of treatment identified in treatability studies or in the literature as indicators of the success of treatment. If the treatment process is not as effective in the

Depending upon the nature of the contaminants present and the treatment objectives, chemical reagents may also have to be incorporated into contaminated surface soils, or injected into deeper contaminated layers, to bring about detoxification or degradation reactions. Such reactions might involve oxidation, reduction, or polymerization, for example. Appropriate reagents, reaction rates, and the leachability and toxicity of reaction products will generally have to be determined by laboratory treatability studies.

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2.5.2 Selection of In-Place Treatment Technology

The assessment of waste, soil, and site-specific variables described above will result in identification of technically feasible in-place treatment technology. Further analysis of each of the technically feasible alternatives is required to determine which (if any) meet the cost-effectiveness criteria of the National Contingency Plan.

The data assembled for assessing technical feasibility should be sufficient to form the basis of initial detailed engineering designs and operating specifications for each in-place treatment system. The designs and specifications in turn form the basis for developing detailed capital, operating and maintenance cost estimates over the lifetime of the remedial program.

The initial implementation plan should then be examined in some detail, and refined as appropriate. Several iterations may be necessary. First, the plan should be examined for completeness and logical consistency with respect to engineering implementation and constructability. Have any steps for successful implementation, operation, and monitoring been overlooked? Are all steps in logical order? Is the schedule realistic? Have all steps been properly costed? Next, an assessment needs to be made of how well each alternative meets the remedial objectives. This may require mathematical modeling of contaminant migration patterns, based on the modified waste/soil system characteristics that would be anticipated if the remedial alternatives were implemented. In addition, any adverse environmental impacts should be identified and assessed. Methods and costs for mitigating these impacts should be incorporated into a revised implementation plan. Finally, each in-place treatment process design that meets the remedial objectives should be rank ordered in terms of annualized cost, and the most cost-effective in-place alternative(s) should be selected for comparison with other alternatives.

2.6 DETERMINATION OF EXTENT OF REMEDY

The process described above, along with a similar process for other technologies, should provide enough information to enable selection of the most cost-effective alternative. The results of the analysis for the in-place treatment alternatives that survive screening are compared with other alternatives that have also been analyzed in detail. The lowest cost alternative that reduces risk to an acceptable level and meets the other objectives of the remedial program is then selected.

2.7 IN-PLACE INFORMATION GAPS

The evaluation of the in-place techniques discussed briefly in this section and in more detail in the next section is hampered by the general lack of information pertaining to remedial applications. The missing information is of two types. The first is general information about the technologies in any setting, remedial action, land treatment, agriculture, and the like. A number of the techniques have been developed for and applied in the latter two areas, but even these are often in the early stages of development.

The second type of information gap is related to specific information on individual technologies. Data on the natural, intrinsic (assimilative) capacity of soil systems to support these in-place technologies are needed, as are data on means to enhance the natural capacity by the addition of reagents, or the modifications of the soil/waste system.

To begin to address some of the information gaps described below, the Utah Water Research Laboratory has initiated studies — in cooperation with the U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory — to investigate in-place treatment of complex hazardous wastes for application to in-place remedial action as well as to land treatment systems. The experimental studies focus on high soil concentrations and assimilation capacities for complex hazardous wastes, and on volatilization of hazardous constituents from soil systems. The goal of the work is to be able to relate waste composition on a constituent basis to soil-treatment capacities. Assimilation capacities with respect to degradation, detoxification, and immobilization will be determined to generate a data base for establishing the capabilities and limitations for soil treatment of hazardous waste constituents.

2.7.1 General Information Gaps

The ability to utilize in-place treatment will be improved by developing a broader data base containing the following:

1) Information obtained from the controlled application of *complex* hazardous wastes (including solid, liquid, and semi-solid wastes) to soil systems in laboratory or field experiments. Information must specifically include mass balance for degradation, mobilization, volatilization, photodegradation, and rates of reaction.

2) Information obtained from *field*-scale applications of hazardous wastes, either controlled or uncontrolled, in which environmental sampling includes waste and soil parameters through the soil profile, soil core and soil pore-liquid, volatile fugitive emissions, and groundwater.

3) Information obtained from controlled experiments on a field scale, comparing effectiveness of adding treatment agents (e.g., chemicals, micro-organisms, adsorbents) compared to a non-treatment agent addition for soil treatment (degradation, transformation, immobilization) of constituents in complex hazardous wastes.

2.7.2 Technology-specific Information Gaps

Several areas in which specific information concerning in-place treatment is scarce or completely lacking have also been identified. These areas relate to the treatment processes in a soil system, viz., degradation, transformation, and immobilization. Such information needed to determine the assimilative capacity, or quantitative ability of the soil system to prevent contamination of air, groundwater, and surface water is described below.

1) Information on soil processes interfacing with atmospheric processes (i.e., controlling volatilization and photodegradation), including:

   - investigation of photochemical reactions that enhance biodegradation of refractory compounds and those that can produce toxic or undesired breakdown products;
   - laboratory and field-scale analysis of the feasibility of using volatilization/photodegradation as a viable treatment method for volatile/photoreactive hazardous chemicals;
   - evaluation of the importance of soil-photochemical reactions to the fate and behavior of photoreactive compounds within the environment;
   - refinement of containment/transport models that address volatilization, vapor adsorption, biodegradation, and leaching through the soil matrix; and
   - continued development of rapid partition coefficient estimation methods for predicting compound partitioning among air/water/soil systems.

2) Information on chemical reactions relating to the transformation and immobilization of constituents in soil systems, including:

- effects of chemical addition (oxidants, reductants, and polymerizing agents) on the soil properties affecting treatment;

- constituent sorption and precipitation studies at concentrations in the soil matrix characteristic of those found at remedial action sites,

- Eh-pH information for metal species in soils at concentrations representative of remedial action site concentrations; and

- behavior of specific metals, viz., arsenic, beryllium, silver, selenium, mercury, and chromium in soil systems, including the investigation of the reaction of chromium (VI) to chromium (III).

3) Information on biological reactions to stimulate the biodegradation of constituents in soil systems, including:

- potential for combinations of chemical and biological treatment methods for accelerating soil treatment;

- potential for composting of hazardous waste contaminated soil for accelerating biological reactions and for detoxifying and degrading recalcitrant organic constituents;

- evaluation of the biodegradation kinetics and extent of hazardous constituents and metabolites of hazardous constituents sorbed to clay and soil organic matter;

- degradation rates and pathways for chemical classes, including alkyl halides and highly chlorinated organics (PCBs) in the soil treatment zone (upper 5 feet of soil); and

- information concerning the effectiveness of micro-organism seeding compared with no seeding, specifically in terrestrial systems.

4) Information on immobilization reactions in the soil/waste system, including:

- investigation of enhancement of sorption by adding different sorbents, such as activated carbon, straw, synthetic resins. (The specific information needed includes application rates of sorbent in relation to concentrations of contaminant in soil);

- continued development of estimation methods for predicting soil adsorption constants by chemical and physical properties of compounds;

- long-term effectiveness of immobilization of sorbed contaminants on soil; and

- effects of solvents on mobility of organic contaminants in soil systems.

5) Information on leaching in the soil/waste system, including:

- laboratory experiments to estimate parameters for transport models that can be used to predict behavior under field conditions;

- field instrumentation to validate transport models under imposed environmental conditions, incorporating the variability under field conditions by designing appropriate sampling stations; and

- effect of different environmental conditions, including soil moisture, redox potential, and organic content on transport parameters.

SECTION 3

TECHNOLOGIES FOR IN-PLACE TREATMENT

3.1 INTRODUCTION

This section presents detailed information on specific in-place treatment technologies. Each technology was selected on the basis of its potential or demonstrated ability to augment natural soil processes to accomplish in-place treatment.

The technology discussions are divided into the five treatment categories presented in Section 2; viz., extraction, immobilization, degradation, attenuation, and reduction of volatiles. Each discussion is presented in the following format:

- Description — a qualitative discussion of the technology and principles on which it is based.
- Wastes amenable to treatment — a discussion of the kinds of wastes suited to the treatment in terms of waste type (organic/inorganic), chemical class, or certain required properties of the class.
- Status of technology — a measure of the availability of the technology and degree to which it has been demonstrated for soil treatment. "Field" means that it has been used for soil treatment in practice, either large-scale or in small pilot studies. "Laboratory" means that the technology has been demonstrated for soil treatment in small experiments in laboratories. "Conceptual" means either that it is still purely theoretical, or that it has been used for treatment other than soil treatment but no laboratory or field work exists for soil treatment.
- Ease of application — a qualitative description of the relative difficulty of implementing the technology in the field. "Easy" means that application problems are not expected under most conditions, while "difficult" means that problems are usually expected. "Easy to difficult" means that ease of application varies considerably, depending on site-specific conditions.
- Potential achievable level of treatment — a description (high, low, variable) of the conceptual or theoretical level of treatment which could be obtained independent of site-specific considerations. A "high" potential achievable level of treatment for reduction, for example, means that wastes applicable to treatment by reducing agents may be effectively degraded by reduction. Site conditions, however, may interfere with technology performance.
- Reliability of method — a brief discussion of the long-term effectiveness of the technology, including reversibility of treatment and retreatment needs. If there is a lack of information on long-term effectiveness, the reliability is designated as "unknown."
- Secondary impacts — a discussion of the effects of technology implementation in addition to its intended primary effect. The impacts discussed include effects on soil properties, site conditions, and the enhancement or retardation of other in-place treatment processes.

- Equipment and exogenous reagents — a brief description of the equipment and materials that may be required to implement the technology. Additional information on equipment and reagents is presented in the appendix.

- Information requirements — a list of information, including waste, soil, and site factors discussed in Section 2, that is needed for application of the technology.

- Sources of information — a listing of the publications used in preparing the technology discussions, including some that are not specifically referenced.

A matrix of important summary information for each of the technologies is presented in Table 3-1.

3.2 EXTRACTION (SOIL FLUSHING)

Description

Removal of soil contaminants can be accomplished through extraction (soil flushing or solution mining). This involves the elutriation of organic and/or inorganic constituents from soil for recovery and treatment. The site is flooded with the appropriate flushing solution and the elutriate is collected in a series of shallow well points or subsurface drains. The elutriate is collected, treated, and/or recycled back into the site. Collection of elutriate is required to prevent uncontrolled contaminant migration through uncontaminated soil and into receiver systems including groundwater and surface water. An example of a soil flushing system with elutriate recycle is given in Figure 3-1.

Flushing solutions may include water, acidic aqueous solutions (sulfuric, hydrochloric, nitric, phosphoric, and carbonic acid), basic solutions (e.g., sodium hydroxide), and surfactants (e.g., alkylbenzene sulfonate). Water can be used to extract water-soluble or water-mobile constituents. Acidic solutions are used for metals recovery and for basic organic constituents, including amines, ethers, and anilines, and basic solutions for metals, including zinc, tin, and lead and for some phenols, complexing and chelating agents, and surfactants (U.S. EPA, 1982).

Addition of any flushing solution to the system requires careful management and knowledge of reactions that may adversely affect the soil system. For example, a sodium addition as sodium hydroxide to soil systems may adversely affect soil permeability by affecting the soil sodium absorption ratio. It is not only important to understand the chemical reaction(s) between solvent and solute, but also between solvent and site/soil system.

For a site contaminated by organic constituents, it may be possible to recycle the elutriate back through the soil for treatment by biodegradation. Proper control of the application rate, based on hazardous waste land treatment principles (U.S. EPA, 1983), would provide for effective in-place treatment at soil concentrations that would allow controlled biodegradation of the waste constituents. Using this approach may eliminate the need for separate processes for treatment and disposal of the collected waste solution, or at least provide for a combination of pretreatment/land application that may be considerably more economical than using unit operations alone for treatment of elutriate.

For soils contaminated with inorganic and organic constituents, a combination of pretreatment land applications where the metal constituent(s) is reduced or eliminated in the elutriate by precipitation, followed by land application of the elutriate, may be a feasible, cost-effective method of treatment.

Soil flushing and elutriate recovery may also be appropriate for situations where chemical oxidizing or reducing agents are used to chemically degrade waste constituents resulting in the production of large amounts of oxygenated, mobile, degradation products. The most conservative and safest approach may be to flush the soil after treatment to recover and possibly reapply the elutriate in a controlled manner to the soil surface.

TABLE 3-1. SUMMARY MATRIX OF TREATMENT TECHNOLOGIES

Technology	Wastes Amenable to Treatment	Status	Ease of Application	Potential Level of Treatment	Reliability
EXTRACTION	Soluble organics and inorganics	Laboratory	Easy – Difficult	Variable	Good
IMMOBILIZATION					
Sorption (heavy metals)					
Agri. products	Heavy metals	Field	Easy – Difficult	High	Retreatment required
Activated carbon	Heavy metals	Conceptual	Easy – Difficult	Unknown	Unknown
Tetren	Heavy metals	Laboratory	Easy – Difficult	High	Unknown
Sorption (Organics)					
Soil moisture	Organics, non-volatile, $K_d < 10$	Conceptual	Easy – Difficult	High	Retreatment required
Agri. products	Organics	Laboratory	Easy – Difficult	High	Retreatment required
Activated carbon	Organics, low water solubility	Field	Easy – Difficult	Low – High	Unknown
Ion Exchange					
Clay	Cationic components	Laboratory	Easy – Difficult	High	Good
Synthetic resins	Certain cationic and anionic compounds	Laboratory	Easy – Difficult	Variable	Unknown
Zeolites	Heavy metals	Conceptual	Easy – Difficult	Unknown	Unknown
Precipitation					
Sulfides	Heavy metals	Conceptual	Difficult	High	Fair
Carbonates, phosphates and hydroxides	Heavy metals	Laboratory	Easy – Difficult	Unknown	Retreatment required
DEGRADATION					
Oxidation					
Soil catalyzed reactions	Aliphatic organics, other organics	Limited field	Easy – Difficult	Variable	Good
Oxidizing agents	Various organics	Limited field	Moderate – Difficult	High	Good
Reduction					
Organics	Chlorinated organics, unsaturated aromatics, aliphatics	Limited field	Easy – Difficult	High	Retreatment required
Chromium	Hexavalent chromium	Limited field	Easy – Difficult	High	Retreatment required
Selenium	Hexavalent selenium	Limited field	Easy – Difficult	High	Retreatment required

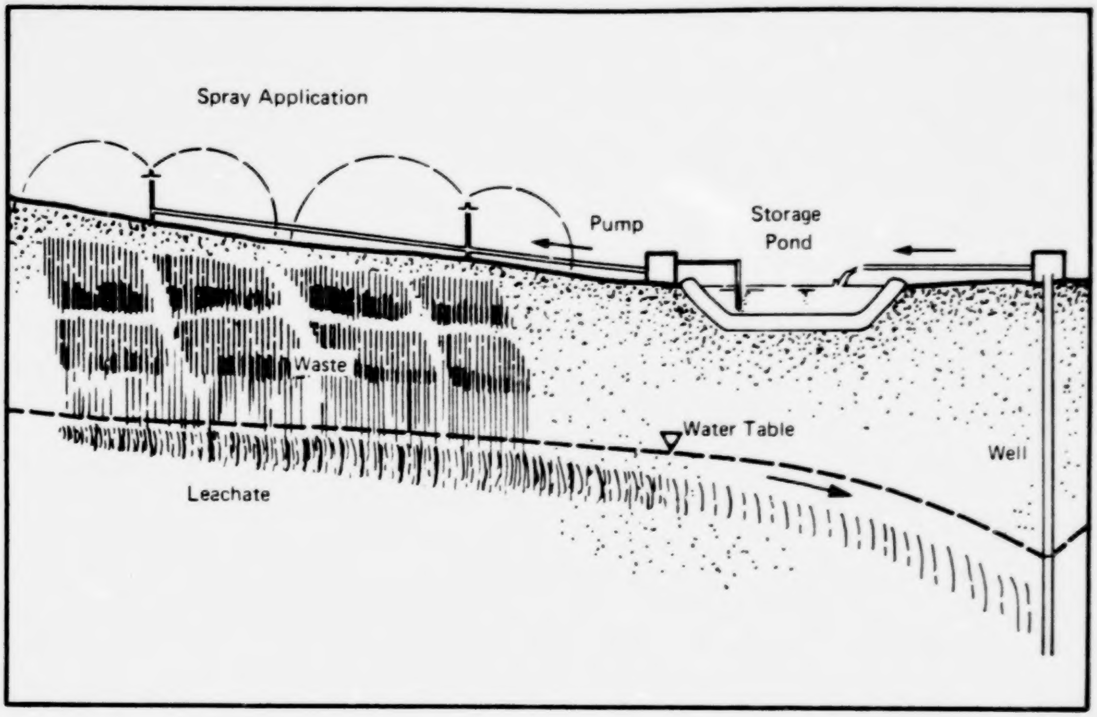
(continued)

TABLE 3.1 (Continued)

Technology	Wastes Amenable to Treatment	Status	Ease of Application	Potential Level of Treatment	Reliability
Sodium reduction	PCB, dioxin, halogenated compounds	Conceptual	Moderate	High	Good
Polymerization	Aliphatics, aromatics, oxygenated organic compounds	Expt. field	Moderate – Difficult	Variable	Unknown
Modification of soil Properties (biodegradation)					
Soil moisture	Organics	Field (Agri.)	Easy – Difficult	Low – High	Retreatment required
Soil oxygen – aerobic	Organics	Field	Easy – Difficult	Low – High	Retreatment required
Soil oxygen – anaerobic	Halogenated organics	Conceptual	Moderate – Difficult	Low – High	Retreatment required
Soil pH	Organics	Field	Easy – Difficult	High	Retreatment required
Nutrients	Organics	Field	Easy – Difficult	High	Retreatment required
Nonspecific organic amendments	Organics, arsenite wastes	Laboratory	Easy – Difficult	Low – High	Retreatment required
Analog enrichment for cometabolism	Some organics with analogs	Laboratory	Easy – Difficult	Low – High	Unknown
Exogenous acclimated or mutant micro-organisms	Various organics	Field	Easy – Difficult	High	Retreatment required
Cell-free enzymes	Organics	Laboratory	Difficult	High	Unknown
Photolysis					
Proton donors	Some organics, including TCDD, Kepone, PCB	Field	Easy – Difficult	High	Unknown
Enhance volatilization	Specific organics	Conceptual	Easy – Difficult	High	Good
ATTENUATION					
Metals	Metals	Field	Easy – Difficult	High	Good
Organics	Organics	Limited field	Easy – Difficult	High	Good
REDUCTION OF VOLATILIZATION					
Soil vapor volume	Volatile organics and inorganics	Laboratory	Easy – Difficult	Low – Medium	Retreatment required
Soil cooling	Volatile organics	Expt., limited field	Difficult	Low – Medium	Retreatment required

Source: Arthur D. Little, Inc.

Figure 3-1. Schematic of an elutriate recycle system.



Source: Ehrenfeld, J.R., and Bass, J.M., 1983.

Wastes Amenable to Treatment

Both inorganics and organics are suitable for soil flushing treatment if they are sufficiently soluble in an inexpensive solvent that is obtainable in a large enough volume. Surfactants can be used for hydrophobic organics.

Status of Technology

This technology is currently at the laboratory stage. Studies have been conducted to determine appropriate solvents for mobilizing various classes and types of waste constituents.

Ease of Application

This technology may be easy or difficult to apply depending on the ability to flood the soil with the flushing solution and the installation of collection wells or subsurface drains to recover all the applied liquids. Provisions must also be made for ultimate disposal of the elutriate.

Potential Achievable Level of Treatment

The achievable level of treatment is variable, depending on the contact of flushing solution with waste constituents, the appropriateness of solutions for the wastes, and the hydraulic conductivity of the soil. This technology is more applicable to highly permeable soils because the level of treatment will probably be higher.

Reliability of Method

Although the level of treatment may be variable, once the waste components are removed from the soil, the treatment is not reversible and no additional retreatment is necessary.

Secondary Impacts

The solutions used for the flushing may themselves be potential pollutants. They may have toxic and other environmental impacts on the soil system and water receiver systems. The soil system after treatment is altered from its original state. Its physical, chemical, and biological properties may be altered adversely; e.g., the pH may be lowered by the use of an acidic solvent, or the soil may be compacted from being flooded. These soil properties may have to be restored to assure that other treatment processes can occur (e.g., biodegradation).

Equipment and Exogenous Reagents

Equipment used for soil flushing include drains and an elutriate collection and distribution system. The solvents for flushing are required.

Reapplication of collected elutriate may require construction of a holding tank for the elutriate.

Information Requirements

- characterization and concentration of waste constituents;
- depth, profile, and areal distribution of contamination;
- partitioning of waste constituents between solvent(s) and soil;
- effects of flushing agent (solvent) on soil physical, chemical, and biological properties;
- suitability of site to flooding and installation of wells and/or subsurface drains;
- trafficability of soil and site.

Sources of Information

Botre, C., et al., 1978; U.S. EPA, 1982, 1983.

3.3 IMMOBILIZATION

3.3.1 Sorption

The sorption of a pollutant refers to processes which result in a higher concentration of the chemical at the surface or within the solid phase than is present in the bulk solution of soils. Actual sorption mechanisms are often not known. Sorption is the major general retention mechanism for many organic compounds and metals. Adsorbed compounds or ions are in equilibrium with the soil solution and are capable of desorption (Bonazountas and Wagner, 1981).

Several processes are involved in sorption including:

- ion exchange,
- physical sorption through weak atomic and molecular interaction forces (van der Waal forces),

- specific adsorption exhibited by anions involving the exchange of the ion with surface ligands to form partly covalent bonds, and

- chemisorption involving a chemical reaction between the compound and the surface of the sorbent.

We will discuss ion-exchange separately as another immobilization technology in Section 3.3.2.

Soil sorption is perhaps the most important soil-waste process affecting immobilization of toxic and recalcitrant fractions of hazardous wastes. Leaching potential and the residence time in soil for constituents which undergo degradation are directly affected by the extent of immobilization.

The sorption process is usually described by an adsorption isotherm, which expresses the relationship between the amount of constituent adsorbed onto a solid (soil, activated carbon, zeolite, organic matter, etc.), and the concentration of solute in solution at equilibrium. One frequently used relationship is the Freundlich isotherm, which is expressed as:

$$S = KC^N \tag{3-1}$$

where

S = amount of constituent adsorbed per unit dry weight of soil,
K and N are constants, and
C = solution phase equilibrium concentration.

The percentage sorbed under natural moisture conditions can be estimated by:

$$\% \text{ sorbed} = \frac{100}{1 + \left(\frac{S}{K}\right)^{1/N} \frac{\Theta}{S}} \tag{3-2}$$

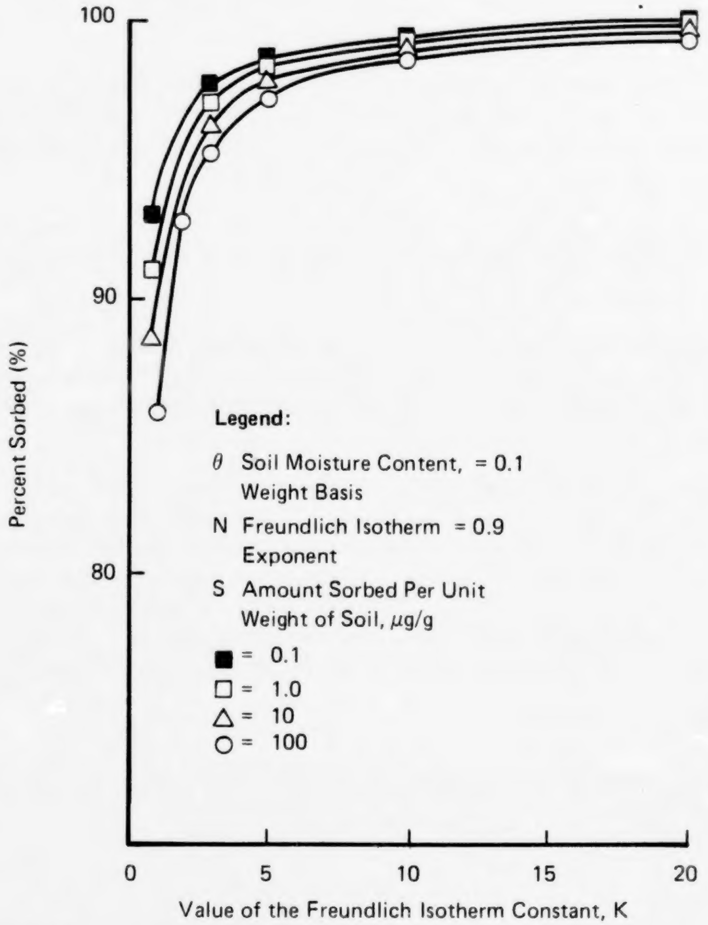
where θ = fraction soil moisture content (weight basis). When the sorption is linear, $N = 1$, and the percent sorbed is not a function of the amount sorbed per unit weight of soil (S). However, when the sorption is not linear, the percent sorbed becomes a function of S. Figure 3-2 shows the percent of chemical sorbed as a function of K values and for different S values.

Desorption of constituents is also important in affecting treatment effectiveness through the extent of release of chemicals from soil into percolating water moving through the soil. Generally the extent of desorption follows the Freundlich isotherm, but with constants different from the ones used for adsorption. This is due to hysteresis of a soil system exhibited during the sorption-desorption cycle. Factors directly associated with desorption include the amount of leachate (soil/water ratio) and the amount of constituent contaminating the soil (soil/constituent ratio). The extent of desorption will decrease with an increase of these ratios.

Treatment techniques to enhance immobilization of constituents by controlling or augmenting the sorption process in soils have been developed based on fundamental principles and applied land treatment techniques. These treatment techniques also provide engineering management tools for affecting treatment of constituents through degradation, especially biological degradation.

Because the mechanisms involved in the sorption of organics are significantly different from that of heavy metals, we will discuss these two groups separately.

Figure 3-2. **Extent of sorption as a function of amount sorbed and K for $\theta = 0.1$ and N = 0.9.**



Source: Mahmood and Sims, 1984.

3.3.1.1 Heavy Metals — Addition of Sorbents

Many heavy metals have a strong affinity for organic matter. The retention of added metals is often well correlated with soil organic matter. Metals are readily chelated and/or complexed by functional groups in organic matter. These include -COOH, phenolic, alcoholic and enolic-OH and carbonyl (C = O) structures of various types. The stability of these metal-organic complexes increases with pH due to the increased ionization of the functional groups. Sorption processes are affected by 1) pH, 2) competing cations, 3) solvent present in a complexed waste, 4) presence of chelating agents, 5) solution ionic strength, and 6) types of anions present in the soil solution.

Theoretically, the addition of organic matter to a contaminated soil should remove metals from the soil solution, thus preventing their leaching in groundwater. Organic materials most conducive for use with soils include: agricultural products and by-products, and activated carbon.

3.3.1.1.1 Addition of Agricultural Products and By-products for Heavy Metals

Description

The use of various agricultural products and by-products, such as straw, sawdust, peanut hulls, and bark, for the removal of heavy metals from wastewater solutions has been recently suggested by Larsen and Schierup (1981) and Henderson et al. (1977 a,b). Larsen and Schierup (1981) found that 1 gram of barley straw was able to adsorb amounts of Zn, Cu, Pb, Ni, and Cd ranging from 4.3 to 15.2 mg, while pine sawdust removed 1.3 to 5.0 mg. The selective order of metal sorption for straw was Pb > Cu > Cd ≅ Zn ≅ Ni. The concentration of metals and the pH value of the metal solutions also affected the amount of metals sorbed. The obvious advantage of the use of waste organic materials compared to the use of other sorbing materials, such as activated carbon, is the lower cost involved when organic waste materials are used.

Agricultural products and by-products (e.g., animal manures, plant residues, and food processing wastes) have been used extensively as soil conditioners. Sewage sludge and animal manures have been used as fertilizer sources and as soil conditioners. The use of such waste materials for the removal of metals in soils has not been extensively studied.

Sewage sludges from municipal areas often contain high concentrations of heavy metals themselves. The use of such sludges should be avoided. Waste materials may also contain soluble organic matter that chelates metals and increases their mobility. More research is needed to identify the extent of increased mobility. Other factors also affect the sorption of metals, including the presence of competing cations and the ionic strength of the soil solution.

To obtain maximum sorption of metals by organic matter, soil pH must be adjusted and/or maintained at greater than 6.5. The addition of organic materials may result in a decreased pH, requiring continued pH adjustment.

Wastes Amenable to Treatment

Heavy metal wastes and organic wastes are amenable to treatment by the addition of organic materials. This discussion is devoted to heavy metals.

Status of Technology

Addition of agricultural materials has been used in the field for soil conditioning. In the laboratory, it has been conceptually evaluated for use in the removal of metals from wastewater.

Ease of Application

The quantity of organic material required cannot be predicted from stoichiometric relationships. Laboratory sorption studies are required. Liming may be required to maintain the pH of the soil system at greater than 6.5. The application process may be easy to difficult depending on the trafficability of the site and the depth of contamination. Thorough mixing is required for maximum waste and organic material contact. Because tilling is used, erosion control techniques may have to be implemented.

Potential Achievable Level of Treatment

This is an effective method for removal of metals from wastes. However, agricultural products and by-products are highly susceptible to microbial activity. Degradation of the materials may result in the release of metals. The long-term level of treatment achievable is probably much smaller than in the short-term unless treatments are repeated.

Reliability of Method

As mentioned above, the mineralization of the organic materials may result in the release of the sorbed metals. Repeated treatments may be necessary periodically. Reliming is likely to be a necessity as well, since mineralization of the organics would tend to reduce the pH of the soil system. Another important factor is the potential competition of the metals with organics which are also sorbable on organic materials.

Secondary Impacts

Organic materials may alter the properties of the soil system including:

- degree of structure;
- water-holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction in soil erosion; and
- soil temperature.

Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material. Since tilling is used to incorporate the organic material into the soil, wind and water erosion may effect the soil surface adversely.

Equipment and Exogenous Reagents

The equipment used are power implements, tillers, and applicators. Organic material and liming materials are the exogenous reagents required.

Information Requirements

- characterization and concentration of metals present in waste;
- depth, profile, and areal distribution of contamination;
- soil pH;
- adsorptive selectivity and capacity of organic material for metals at the site;
- soil biological activity (mineralization potential of organic material); and
- trafficability of soil and site.

Sources of Information

Bonazountas, M., and Wagner, J., 1981; Brown, L.S., 1972; Coffey, D.L., and Warren, G.R., 1969; Coun. for Agri. Sci. & Tech., 1975; Damanakis, M., et al., 1970; Jacobs, L.W., 1977; Ko, W.H., and Lockwood, J.L., 1968; Shin, Y., et al., 1970; Tames, R.S., and Hance, R.J., 1969; Taylor, J.M., et al., 1980; U.S. EPA, 1976, 1977, 1978, 1980 1981; Voerman, S., and Tammes, P.M. 1969; Walker, A., and Crawford, D.V., 1968.

3.3.1.1.2 Addition of Activated Carbon for Heavy Metals

Description

In water and wastewater treatment, most of the research and development effort related to the use of activated carbon is oriented toward organics, with relatively little attention being given to inorganics, specifically heavy metals. The soil literature lacks information on the use of activated carbon as a treatment method. The following discussion is based on the use of activated carbon in water treatment.

Several factors can contribute to heavy metal removal capability of activated carbon: 1) specific surface area, 2) pore size and distribution, and 3) surface chemical properties. Huang and Ostoric (1978) suggested that the chemical reactivity of the surfaces is of major importance. They found that, in general, powdered activated carbon (e.g., Nuchar S-N and Nuchar S-A) has a low pH at the zero point of charge (zpc) (Table 3-2) and excellent sorption capacity for heavy metals. Granular activated carbon (e.g., Darco HD 3000 and Filtrasorb 400), having a high pH_{zpc} is rather poor for metal ion adsorption. The pH_{zpc} value reflects the acidic nature of surface functional groups.

The effect of solution pH on Cd sorption by Nuchar-SA is illustrated in Figure 3-3. The data were obtained from a batch equilibrium study using a synthetic Cd-fluoroborate-plating wastewater and activated carbon (Huang and Smith, 1981). The initial linear segments illustrate that sorption of Cd by Nuchar-SA increases with pH. Above pH 6 to 7, precipitation reactions, $CdCO_3$ and $Cd(OH)_2$, become the major mechanism of removal of Cd from solution. Precipitation reactions have long been used as the method of removing metals from wastewater. Precipitation is often, however, a kinetically slower process than sorption.

Larsen and Schierup (1981) found that granular activated carbon removed from solution 6.2 to 19.5 mg of Zn, Cu, Pb, Ni, and Cd per g of carbon.

Figure 3-4 illustrates the extent of Cd sorption as affected by the carbon to cadmium ratio. Huang and Smith (1981), using these data, recommended a carbon-to-metal ratio of 0.25 g/mg at pH 7 for maximum efficiency of removal of Cd from wastewater. Work by Pillie et al. (1975) indicates that carbon-to-metal ratios of 0.1 g/mg are needed for maximum efficiencies in treating wastewater. Soils may require ratios in excess of this amount because sorption is affected by numerous factors, such as the presence of chelating agents, competing cations, and ionic strength of the soil solution. Sorption of metals by activated carbon occurs over a wide pH range, with maximum efficiency at a pH greater than 6.5. Adjustment of the pH of acid soils with liming materials may be necessary.

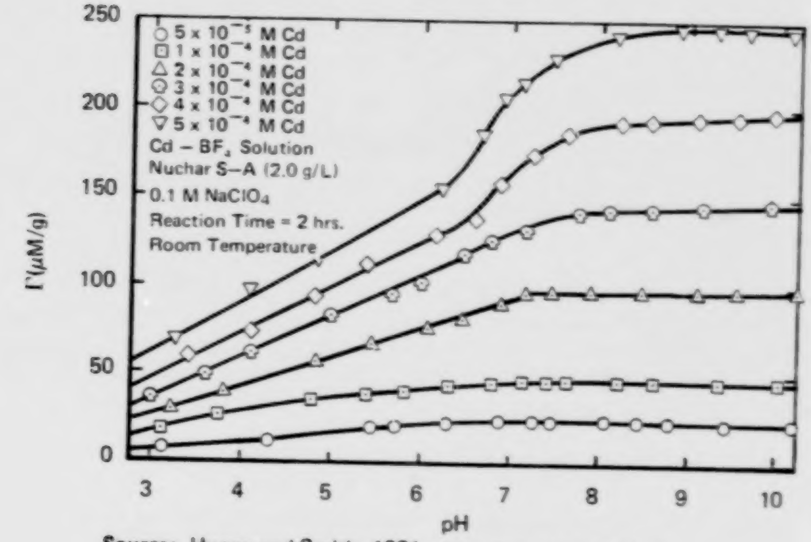
TABLE 3-2. TYPICAL SURFACE PROPERTIES OF ACTIVATED CARBONS

Carbon Type	Specific Surface Area (m^2/g)	Particle Size (mm)	pH_{zpc}
Nuchar S-N	1400-1800	0.04-0.10	5.84
Nuchar S-A	1400-1800	0.03-0.10	3.84
Darco HD 3000	550-650	0.84-4.75	a
Filtrasorb 400	941	0.90-1.00	7.10

a. Value not determined, but estimated to be 5-7 based on comparison with values of other Darco brand granular carbons and observations of pH drift in various solution.

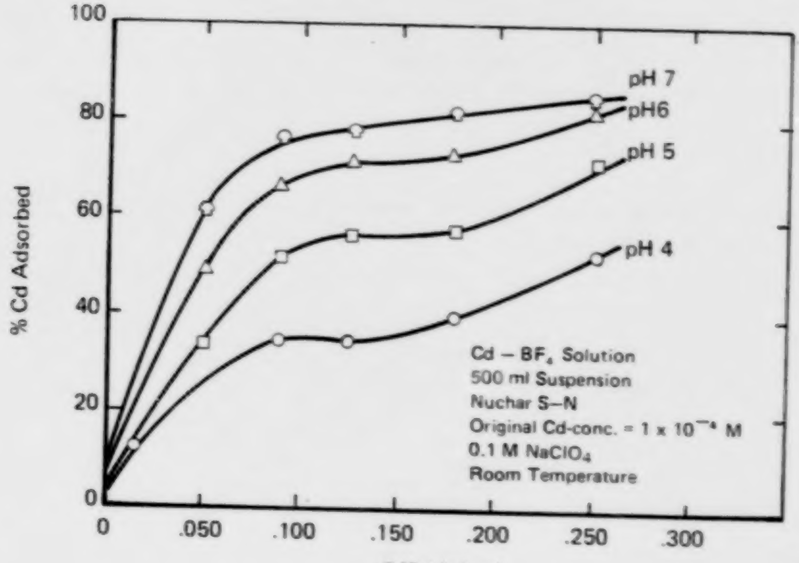
Source: Huang and Smith, 1981. (See Copyright Notice)

Figure 3-3. **Adsorption characteristics of Cd(II) from synthetic Cd(II)-plating wastewaters (Cd-BF_4 solution) as affected by pH.**



Source: Huang and Smith, 1981. (See Copyright Notice)

Figure 3-4. **Extent of Cd(II) adsorption as affected by carbon/cadmium ratio at various pH.**



Source: Huang and Smith, 1981. (See Copyright Notice)

Activated carbon should be relatively resistant to degradation in the soil environment.

Wastes Amenable to Treatment

Heavy metal wastes (and organic wastes) are amenable to treatment with activated carbon.

Status of Technology

This technology is used conventionally in wastewater treatment, but its use in soil treatment is still conceptual in nature.

Ease of Application

Liming may be necessary to keep the soil in the pH range of optimum sorption. The application of this technology is easy to difficult, depending on the trafficability of the soil and site and the depth of contamination. Thorough mixing is required for maximum contact between the waste and the activated carbon. Because of the tilling that is required for incorporation of the activated carbon into the soil, controls to prevent erosion from runoff and controls for runon may have to be installed, depending on the site.

Potential Achievable Level of Treatment

This technology has been effective in wastewater treatment. However, removal efficiency is metal-specific. The potential achievable level of treatment for metals in soil is unknown because of competition with organics and because of the number of complicating variables in the soil system.

Reliability of Method

The reliability of this method is unknown. Desorption may be a problem in the long term because of competition for the activated carbon by organics in the soil. Also, changes in pH in the soil will affect the sorption. Reliming may be necessary to keep the metals adsorbed on the activated carbon.

Secondary Impacts

Tilled soils are usually more susceptible to water and wind erosion.

Equipment and Exogenous Reagents

The equipment needed includes power implements, tillers, and applicators. Activated carbon and liming materials are the exogenous reagents used.

Information Requirements

- characterization and concentration of metals present in waste;
- depth, profile, and areal distribution of contamination;
- soil pH;
- adsorptive selectivity and capacity of activated carbon for metals at site;
- zero point of charge of activated carbon;
- trafficability of soil and site.

Sources of Information

Huang and Astoric, 1978; Huang and Smith, 1981; Pillie et al., 1975.

3.3.1.2 Heavy Metals — Chelation with Tetren

Description

Metals will react with tetraethylenepentamine (tetren) to form stable metal chelates. Most chelating agents, such as EDTA, will increase metal mobility in soils and their use is to be avoided. Metal complexes with tetren are, however, strongly sorbed by soil clays, thus immobilizing the metal by enhancement of the natural soil sorption system. Smeulders et al. (1983) showed that the use of tetren increases the extent of metal sorption by soil clays. Their study indicated that the addition of tetren to a clay soil ensures the nearly complete sorption of rather large doses of Cu, Zn, Ni, and Cd, with efficiencies comparable to those for specific adsorption (which is restricted to a very small fraction of the exchange capacity).

To be effective, tetren must be applied to a soil relatively high in clays. Tetren-metal complexes are not sorbed by soil organic matter. If tetren is applied to an organic soil low in clays, the tetren-metal complex will remain in the soil solution and will be susceptible to leaching.

It is possible that the utility of tetren in adsorption to clay-like soils is due to the presence of metallic ions, such as iron, in the clay. To obtain a better understanding of the long-term stability of the tetren-metal complexes, it will be necessary to determine the prevalent form(s) of the complex for each metallic species.

It is possible, for example, to form a complex with a metal ion in which several of the amine groups in one tetren molecule are bonded to the same metal ion. Alternatively, only the terminal amine group (or possibly only the secondary amine groups) may be available for coordination to the metal of interest. The question of single versus multiple coordination of the amines to the metal of interest is extremely important, since it directly affects the effective stability of the resultant complex. For example, if multiple amines are coordinated to a single metal ion, exchange processes that remove only one amino group will not result in mobility of the metal ion. Indeed, if it is held by the remaining amino group coordination, subsequent exchange to permit recomplexation of the displaced amine group is still possible.

In addition, the question of complex type is also important with respect to adsorption to the clay materials. The higher the number of amine groups that are complexed to the clay substrate, the fewer there are available for the metal ion of interest. Tetren is a molecule which maximizes the number of amine groups available for metal complexation in a small stereochemical area, and deserves further study as a fixation method for metals known to form strong amine complexes.

The stability of tetren-metal complex against decomposition or degradation is not yet known. More research is also needed on soil factors affecting metal complexation with tetren and resulting sorption by clays, including soil moisture, pH and the ionic strength of the soil solution.

Wastes Amenable to Treatment

Heavy metal wastes are amenable to treatment with tetren. Tetren will likely form strong complexes with those metallic species that interact strongly with amines.

Status of Technology

There have been limited studies in the laboratory and greenhouse. It is still at the conceptual stage in the field. The stability of the tetren-metal complex against decomposition and degradation is not yet known. The soil factors affecting metal complexation with tetren and the resulting sorption of the complex by clays are not well understood. These soil factors probably include soil moisture, pH, and the ionic strength of the soil solution.

Ease of Application

Tetren should be added in sufficient amounts for the formation of a 1:1 complex with the metals present. To ensure the formation of such a complex, a ratio of at least 1:1.15 metal/tetren is advisable. Addition of clay materials may be necessary to increase sorption of tetren-metal complex. Liming may also be necessary if the soil is too acidic. The application may be easy to difficult, depending on the trafficability of the soil and the site and the depth of contamination. Thorough mixing is required for maximum contact between the waste and the tetren. Erosion and runon controls may be necessary because the tilling of the site may increase its susceptibility to erosion.

Potential Achievable Level of Treatment

The achievable level of treatment is potentially high, depending on the characteristics of the soil at the site and the complexation capacity of tetren for the metals present at the site.

Reliability of Method

The stability of the tetren-metal complex is not yet known. Also, its interaction with soil factors like soil moisture, pH, and soil ionic strength is not known. These uncertainties affect the predictability of the tetren-metal complexation effectiveness in soil. If tetren is applied to a soil low in clays, the tetren-metal complex will remain in solution and be susceptible to leaching. In general, this technology cannot be considered reliable at the present time.

Secondary Impacts

Tilling of the soil to incorporate the tetren may increase the susceptibility of the site to erosion by wind and water.

Equipment and Exogenous Reagents

Equipment needed for the application of this technology includes power implements, tillers, and applicators. Tetren and liming materials are required. If the soil at the site is low in clay, it might be necessary to incorporate clay as well.

Information Requirements

- characterization and concentration of metals present in waste;
- depth, profile, and areal distribution of contamination;
- soil pH;
- complexation capacity of tetren with metals at site;
- clay content of soil at site;
- organic matter content of soil at site;
- degree of sorption of tetren-complex with soils at site;
- trafficability of soil and site.

Sources of Information

Smeulders et al., 1983.

3.3.1.3 Organics — Reduction of Soil Moisture

Description

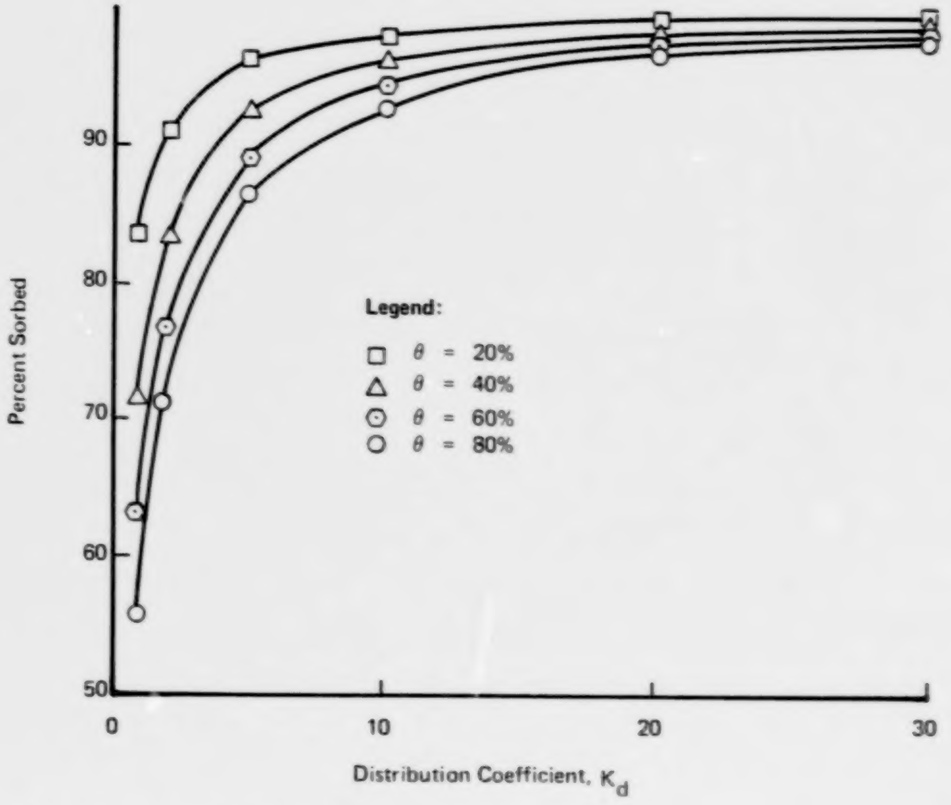
Controlling the moisture content of a soil can be utilized to immobilize constituents in contaminated soils, as well as allowing for additional time to accomplish biological degradation. Where immobilization of constituents using this technique is to be followed by anaerobic decomposition in a treatment train, anaerobiosis must be achieved with techniques other than flooding, such as soil compaction or organic matter addition.

Using the Freundlich isotherm, discussed previously, the percent sorbed under natural moisture conditions can be estimated by using Equation 3-2 (see subsection 3.3.1). When N is equal to 1 (i.e., linear isotherm), Equation 3-2 becomes:

$$\% \text{ sorbed} = \frac{100}{1 + (\Theta/K_d)} \qquad (3\text{-}3)$$

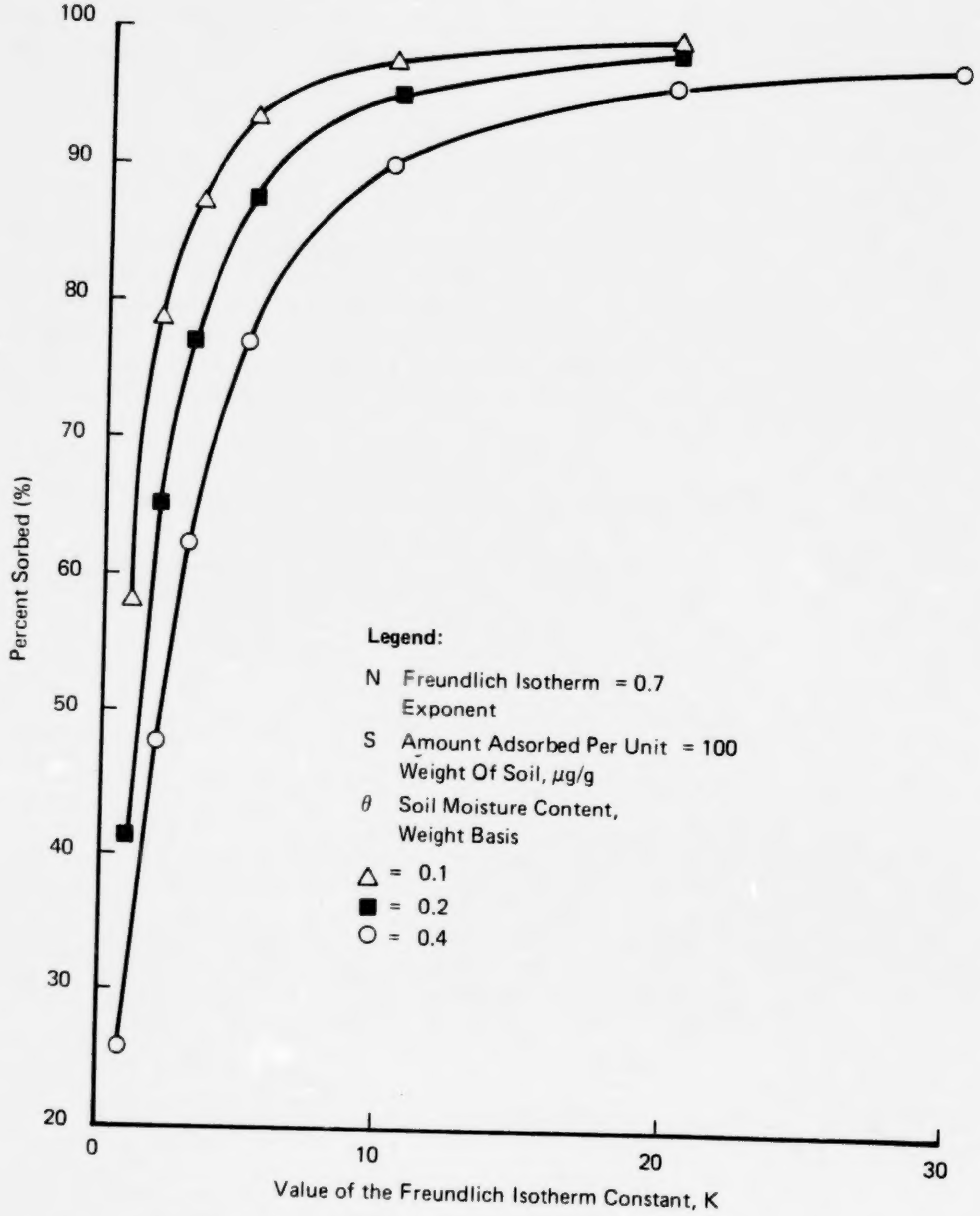
where K_d is the distribution coefficient of the chemical between soil and soil water and θ is the soil moisture content (weight basis). Figure 3-5 shows percent sorbed as a function of K_d for different values of θ. From Figure 3-5, it is seen that with lower moisture content, the percent of adsorbed chemical is higher. This is especially important for constituents with relatively small K_d values, i.e., constituents not strongly sorbed to soil. When the adsorption isotherm is nonlinear ($N < 1$) for a given amount sorbed per unit weight soil (S), controlling soil moisture will also follow the same trend as in the case of the linear isotherm, as shown in Figure 3-6.

Figure 3-5. Extent of sorption as a function of soil moisture θ and K_d.



Source: Mahmood and Sims, 1984.

Figure 3-6. **Extent of sorption as a function of amount sorbed and K for a range of moisture contents and N = 0.7.**



Source: Mahmood and Sims, 1984.

Wastes Amenable to Treatment

This technology is more effective for those organics that are not strongly sorbed (K_d less than 10) than for those that are strongly sorbed. However, the wastes must not be volatile, as drying of the soil will increase volatilization.

Status of Technology

This technology is conceptual at this point in time.

Ease of Application

The site may require tillage to incorporate wastes and to enhance soil drying. Installation of a drainage system may be necessary to reduce soil moisture. Measures to increase soil temperature may enhance soil drying (see Section 4). Theoretically, this is a simple technology that would be easy to apply. However, difficulties that could make it difficult to maintain low soil moisture may arise at the site.

Potential Achievable Level of Treatment

With suitable characteristics of the waste, soil, and the site, the achievable level of treatment may be potentially high.

Reliability of Method

This method is totally reversible. To maintain an effective low level of soil moisture, constant maintenance of the drainage system and tilling is necessary.

Secondary Impacts

Decreased soil moisture may result in possible retardation of microbial activity and increased volatilization of volatile waste components. Clay-catalyzed degradation may be enhanced, and a reduction of toxic concentrations due to volatilization may enhance microbial activity if the concentrations were toxic initially. Tilling will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

No exogenous reagents are required. Equipment for drainage, tillage, and power implements are necessary.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- depth, profile, and areal distribution of contamination;
- sorption based on organic carbon content (K_{oc});
- octanol/water partition coefficient (K_{ow});
- distribution coefficient (K_d);
- soil moisture (θ);
- soil pH;
- trafficability of soil and site.

Sources of Information

Mahmood and Sims, 1984.

3.3.1.4 Organics — Addition of Sorbents

Organic matter can be used to sorb organics in soil. Sorbents may immobilize the organic constituents, and may also allow additional time for further treatment by biodegradation. Addition of an adsorbent is also useful for relatively "immobile" compounds if cracks and fractures exist in the soil which may increase the potential for mobilization and groundwater contamination. The sorbents which can be used in soils include agricultural products and by-products, sewage sludges, other organic matter and activated carbon.

3.3.1.4.1 Addition of Agricultural Products and By-Products, Sewage Sludges, and Other Organic Matter

Description

Addition of organic matter including sewage sludge, agricultural products and by-products, and organic soil materials to a site/soil/waste system increases the organic content of the soil. This is useful both for waste attenuation (see Section 3.5) and for immobilizing organics in wastes by sorption. Addition of organic matter for increasing the sorption capacity for toxic constituents is especially important and effective in soils with low organic matter content, such as sandy and strip-mined soils.

Sludge may be defined as a semi-liquid waste having a suspended solid content ranging between 0-25 percent dry solids. Sewage sludges are generated by different processes during wastewater treatment. They may be classified either according to stage of treatment (e.g., primary, secondary, tertiary), or according to the process by which the sludges were produced (e.g., activated, digested, etc.). Municipal sludges contain organic and inorganic fractions with 90 percent by weight or more water. Average sludge characteristics of primary and digested sludge are shown in Table 3-3. However, it should be realized that sewage sludge characteristics are quite variable, depending on the source and type of industries associated with the makeup of wastewater (Table 3-4).

Additional advantages of using municipal sludges in organic waste treatment are:

1. Sewage sludges contain active indigenous populations of micro-organisms with degradative potential. This enhances the possibility of degrading toxic constituents.

2. Sewage sludges provide necessary nutrients for biodegradation.

A major disadvantage of using sewage sludges is that the heavy metal content of the sludge may increase potential for groundwater pollution. Therefore, careful management practices are required in terms of application rates of sludges that have high levels of heavy metal. Table 3-5 shows the accumulation of metals allowed in agricultural land (assuming it is safe with respect to leaching), based on the cation exchange capacity (CEC) of the soil.

Organic materials have been added to soil systems to increase sorptive capacity for pesticides. Walker and Crawford (1968) added straw to different soils and noticed an increase in adsorption of four s-triazine herbicides (atrazine, propazine, prometone, and prometryne). The application rate to achieve immobilization was the amount necessary to raise the organic matter content of soil to 2.5 percent. If an organic content of soil of 0.5 percent is assumed, the amount of straw needed is 2 percent or 20,000 ppm, and if a 6-inch depth of incorporation is assumed, the application rate is 45 tons/hectare. The adsorption capacity of soil mixed with the straw remained constant for 81 weeks.

Other materials that have been investigated include plant roots, muck soil, fungal mycelium, and baker's yeast. Tames and Hance (1969) have shown that the addition of freshly killed roots of five plants (oats, beans, peas, cucumber, and radish) to soil increased its adsorptive capacity. The study was conducted with the herbicides atrazine, diuron, linuron, and monolinuron. The adsorptive capacity of the plant roots, however, was less than the capacity of soil organic matter. Coffey and Warren (1969) used a muck soil in the adsorption of several herbicides. With low

TABLE 3.3. AVERAGE CONCENTRATION OF CONSTITUENTS IN PRIMARY AND DIGESTED SLUDGES FROM 33 U.S. TREATMENT PLANTS.

Constituent	Raw or Primary (geometric mean[a])	Digested or Stabilized (geometric mean[a])
	mg/kg except where noted	
Nitrogen	80,000	37,100
Phosphorus	9,070	16,700
Sulfur	3,100	6,010
Boron	775	380
Cadmium	27	4.3
Cobalt	410	290
Copper	740	1,270
Mercury	8.2	6.5
Manganese	460	475
Nickel	420	530
Lead	1,150	2,210
Silver	355	190
Strontium	175	290
Zinc	1,740	2,900
% Volatile Solids	74.4	51.9
Btu/lb (heat of combustion)	7,910	5,850

a. The *nth* root of the product of *n* observed values.

Source: Jacobs, L.W., 1977.

TABLE 3-4. ELEMENTAL ANALYSES OF TREATMENT PLANT SLUDGE SAMPLES EXPRESSED AS RANGES ON A DRY WEIGHT BASIS (in mg/kg)[a]

Chemical Element	Domestic Wastewaters	Industrial and Domestic Wastewaters	Industrial Wastewaters
Phosphorus	2,900-19,600	11,000-22,800	12,700-38,300
Calcium	4,100-120,000	13,200-40,000	32,000-128,000
Magnesium	500-5,400	2,700-4,300	3,000-7,600
Potassium	400-6,000	700-1,700	1,600-4,000
Sodium	200-7,000	500-2,300	800-5,400
Iron	2,300-12,600	15,320-47,600	64,500-225,000
Aluminum	3,800-13,400	3,850-12,000	10,800-70,000
Zinc	1,000-1,800	800-4,600	3,200-14,000
Copper	95-700	960-2,300	1,640-4,700
Nickel	110-400	200-900	440-2,800
Cadmium	<10-400[b]	90-240	<40-200
Manganese	100-300	500-6,100	640-6,100
Chromium	50-200	260-2,650	1,240-2,700
Cobalt	20-<400	400-500	<40-500
Lead	200-<500	760-2,790	1,280-8,300
Silver	7-100	20-300	200-1,680
Strontium	100-200	100-1,600	80-2,100
Beryllium	<10-<100	<10-<100	<40-<100
Vanadium	<500-1,000	<200-500	100-2,000
Barium	600-1,000	700-1,350	2,600-6,400
Boron	50-400	c	c
Mercury	1.0-11.2	2.6-5.0	0.6-3.0

a. EPA analysis data – sludges collected from four plants for each type of wastewater received, 12 treatment plants in all.

b. An unusually high value for Cd obtained from only one sludge source.

c. Analyses not included.

Source: Jacobs, L.W., 1977.

TABLE 3-5. TOTAL AMOUNT OF SLUDGE METALS ALLOWED ON AGRICULTURAL LAND

Metal	**Soil Cation Exchange Capacity (meq/100g)[a]** <5	 5-15	 >15
	Maximum amount of metal (lb/acre)		
Lead (Pb)	500	1,000	2,000
Zinc (Zn)	250	500	1,000
Copper (Cu)	125	250	500
Nickel (Ni)	50	100	200
Cadmium (Cd)	5	10	20

[a] Determined by the pH 7 ammonium acetate procedure.

Source: Jacobs, L.W., 1977.

TABLE 3-6. EFFECT OF INCREASING THE CONCENTRATION OF MUCK SOIL AND BENTONITE CLAY ON THE ADSORPTION OF HERBICIDES

Herbicide	**Control (No Adsorbent)**	**Concentration of Herbicide in ppm to Give 50% Root Inhibition of the Test Plant** **0.01%** **Muck**	 **Bentonite**	 **1.0%** **Muck**	 **Bentonite**
2,4-D	0.12	0.13	0.12	0.43	0.12
DNBP	30	37	34	83	36
Amiben	6.8	6.8	8.3	11	8.3
DCPA	10.5	10.5	10.5	38	10.5
Dipheramid	1.4	1.4	1.4	4.3	5.1

Source: Coffey, D.L., and Warren, G.F., 1969. (See Copyright Notice)

adsorbent concentrations added to the growth medium (0.01 percent), negligible adsorption was observed for muck soil. However, when the concentration was increased to 1.0 percent, adsorption was increased for muck soil (Table 3-6). Ko and Lockwood (1968) have shown that addition of living mycelium *(R. Solani)* to oxidized soil restored its ability to immobilize PCNB and dieldrin. Shin et al. (1970) also demonstrated the beneficial effect of mycelia *(R. Solani)* on soil sorption of DDT. Voerman and Tammes (1969) demonstrated effective sorption of lindane and dieldrin by baker's yeast. With yeast and mycelia cells, nonliving cells exhibited greater sorption capacity than living cells.

Wastes Amenable to Treatment

Organics are amenable to sorption by organic materials.

Status of Technology

Laboratory studies have been conducted demonstrating the sorptive capacity of various organic materials.

Ease of Application

Organic material may be ground, if necessary, and applied to the soil surface or injected below the surface and thoroughly mixed with the contaminated soil. Controls to prevent runoff and runon of precipitation may be necessary. This technology is therefore easy to difficult to apply, depending on the trafficability of the soil and site and the depth of contamination.

Potential Achievable Level of Treatment

The level of treatment achievable is potentially high.

Reliability of Method

Periodic treatment may be required if wastes are recalcitrant. Mineralization of organic materials may release waste constituents if the additives biodegrade more quickly than the waste.

Secondary Impacts

Organic materials may affect soil properties, including:

- degree of structure;
- water-holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction in soil erosion potential;
- soil temperature.

Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material. Tillage may make the site more susceptible to water and wind erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are required. Organic materials are the only exogenous reagents required.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- depth, profile, and areal distribution of contamination;
- adsorption isotherm constants for specific added organic material (K, N);
- soil pH;
- soil biological activity (soil C:N:P ratio, soil oyxgen content, soil moisture, etc.);
- trafficability of soil and site.

Sources of Information

Jacobs, 1977; Walker and Crawford, 1968; Tawes and Hance, 1969; Coffey and Warren, 1969; Ko and Lockwood, 1968; Shin et al., 1970; Voerman and Tammes, 1969.

3.3.1.4.2 Addition of Activated Carbon for Organics

Description

Activated carbon is a very strong sorbent for certain classes of chemicals and has been used extensively in industrial and advanced domestic wastewater treatment processes. The aggregate structure of activated carbon (i.e., the pores distributed as macropores (channels) and micropores (capillaries)) enhances its ability for adsorption. Powdered activated carbon is the preferred form because of its high surface area to mass ratio (~ 1000 m^2/g). Per unit mass of activated carbon, the powder form offers the advantages of maximum rate of sorption, ease of mixing with the soil, and maximum extent of contact of waste constituents with carbon.

One assumption used to determine an application rate for activated carbon is that the amount of activated carbon needed to make constituents unavailable for plant uptake will be enough to immobilize the constituent. Use of this assumption allows a starting point based on several examples from the literature for short-term treatability studies with site/soil/waste systems. However, it should be recognized that the amount of activated carbon required varies with type and amount of constituent and plant involved. Much more research is required with hazardous waste constituents in different site/soil/waste conditions to develop a useful data base for designing efficient treatability studies and for determining effective activated carbon application rates.

Activated carbon has been used to reduce phytotoxicity and uptake of pesticides from soil by crops (Ahrens and Kring 1968; Andersen 1968; Lichtenstein et al., 1968; Coffey and Warren, 1969; Gupta, 1976; Weber and Mrozek, 1979; Strek et al., 1981). Application rates for the compounds used in these studies including PCB's, aldrin, dieldrin, heptachlor, heptachlor epoxide, atrazine, monuron, bromacil, DPCA, DMPA, CIPC, and trifuralin, varied from 1 to 7 metric ton/hectare. Cost calculations were based on high application rates. For pesticide chemicals, it was demonstrated that activated carbon was more effective on non-ionic compounds, and that adsorption was sustained for long periods of time, with negligible desorption. However, for ionic compounds, desorption may be significant.

Requirements for activated carbon for other constituents (kg activated carbon per kg constituent) are 10-20 kg/kg for toluene and 10-100 kg/kg for sodium dodecyl benzene sulfonate (Jensen, 1982). Activated carbon sorption for a large number of energy processes related pollutants, based on the Freundlich isotherm model, is included in the U.S. EPA publication, "Carbon Adsorption Isotherms for Toxic Organics" (Dobbs and Cohen, 1980).

Wastes Amenable to Treatment

Organic wastes, particularly high molecular weight compounds with low water solubility, low polarity, and low degree of ionization, are amenable to treatment with activated carbon. This treatment has been used on pesticides. Activated carbon is more effective with non-ionic than ionic compounds. Highly water soluble organics, which often contain two or more hydrophilic groups, are difficult to remove using activated carbon.

Status of Technology

In the field, activated carbon has been used to immobilize pesticides and herbicides in soils. The long-term physical and chemical stability of activated carbon in soil systems is unknown.

Ease of Application

Activated carbon may be applied to the soil surface and thoroughly mixed. Wind conditions must be assessed during application to avoid blowing of carbon. The carbon should be applied during periods of low wind activity or wetted before application. Alternatively, the carbon may be injected below the soil surface and then thoroughly mixed with the soil. Activated carbon has been used to immobilize pesticides at rates of 1-7 metric ton/hectare. The ease of application depends on the trafficability of the soil and the site and the depth of contamination. Controls to prevent runoff and runon may be necessary because erosion could be a problem.

Potential Achievable Level of Treatment

The level of treatment achievable is dependent on the sorptive capacity of activated carbon for the specific waste constituents present at the site and the extent of contamination. The treatment achieved may range from low to high.

Reliability of Method

As mentioned earlier, the long-term physical and chemical stability of activated carbon in soil systems is unknown. Because it has been used in the field successfully for pesticides, it may be considered reliable at least in the short run. Desorption may be a problem for ionic compounds because of competition with non-ionic compounds which may be present in the soil.

Secondary Impacts

Immobilization of organics by activated carbon may adversely affect the rate of biodegradation in soils. Tillage will increase the susceptibility of the site to water and wind erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are needed to apply the activated carbon.

Information Requirements

- characterization and concentration of wastes, particularly organic at site;
- depth, profile, and areal distribution of contamination;
- soil pH;
- adsorptive selectivity and capacity of activated carbon for metals at site;
- adsorption isotherm constants (K, N) for specific waste constituents;
- trafficability of soil and site.

Sources of Information

Ahrens, J.F., and Kring, J.B., 1968; Andersen, A.H., 1968; Lichenstein, E.P., et al., 1968; Coffey D.L., and Warren, G.F., 1969; Gupta, O.P., 1976; Weber, J.B., and Mrozek, Jr., E., 1979; Strek, H.J., et al., 1981; Jensen, R.A., 1982; Dobbs, R.A., and Cohen, J.M., 1980.

3.3.2 Ion Exchange

Ion exchange is a process in which certain minerals and resins in contact with a solution, particularly an aqueous one, release ions in preference for ions of another type present in the solution. Clay minerals in soil can remove cations in exchange for an equivalent amount of calcium. Ion exchangers can be classified into two principal types: cationic and anionic. Cation exchangers have replaceable cations which are exchanged for other cations in the waste.

TABLE 3-7. CATION EXCHANGE CAPACITY (CEC) FOR VARIOUS MATERIALS

Material	CEC Value (m.e./100g)
Humus	200
Montmorillonite	100
Vermiculite	150
Hydrous Mica and chlorites	30
Kaolinite	8
Hydrous oxides	4

Source: from Brady, N.C., 1974.

Correspondingly, anion exchangers have replaceable anions which are exchanged for other anions in the waste. Three types of ion exchangers will be discussed below as technologies usable in soils for immobilization of pollutants in soil. They are: clays, synthetic resins, and zeolites.

3.3.2.1 Addition of Clays

Description

Clays have high surface areas and are especially effective in immobilizing cationic compounds. A mixture of clay and organics could be used for wastes containing both ionic and hydrophobic compounds. The cationic exchange capacity (CEC) of a soil is usually defined as the number of milliequivalents of the ion that can be exchanged per 100g dry weight of soil. With clays, the exchanged ion is often calcium:

$$M^{++} + [\text{clay}] . \text{Ca} \rightleftarrows \text{Ca}^{++} + [\text{clay}] . M \qquad (3\text{-}4)$$

Among soils, humic material and clays tend to have the highest CEC values. Typical CEC values for various materials are shown in Table 3-7. Brady (1974) also showed a range of CEC values between 2-60 m.e./100g for various soils. The cation exchange capacity is variable in a particular soil; in most soils the exchange capacity increases with pH (Brady, 1974).

Bentonite clay (primarily montmorillonite) has been used for inactivating pesticide phytotoxicity (Coffey and Warren, 1969). Table 3-8 illustrates the sorption of herbicides by bentonite clay at a clay concentration of 25 mg/25 ml solution. As expected for pesticides in anionic form (Weber et al., 1965), neither amiben nor 2,4-D were sorbed. Paraquat, a strongly cationic and water-soluble chemical, was strongly sorbed by bentonite. Paraquat cations penetrate the basal plane of the bentonite, and sorption is relatively irreversible. Hydrogen saturated montmorillonite exhibited greater adsorption than sodium saturated montmorillonite for pesticides including S-triazines, substituted ureas, phenyl carbamates, anilines, anilides, and picolinic acids (Bailey et al., 1968).

Wastes Amenable to Treatment

Cationic compounds, both organic and inorganic are amenable to this treatment. This technology is not effective if the cations to be immobilized are present in the wastes in relatively low concentrations when compared to certain other cations (e.g., Ca^{++}, Na^{+}, Fe^{++}, and K^{+}). The latter cations may overwhelm the exchange capacity of the clay and low concentrations of the former cations, including those with higher affinities, will not be significantly exchanged. Landfill leachates and industrial wastes are often concentrated solutions with high total dissolved solids content (including Na^{+}, Ca^{++}, etc.). Trace cations may not be effectively exchanged in these wastes. For heavy metals, a high pH (greater than 7) would limit the role of ion exchange in preference for precipitation (Bonazountas and Wagner, 1981).

TABLE 3-8. CONCENTRATIONS IN PPM OF HERBICIDE SOLUTIONS ADDED TO THE ADSORBENTS TO GIVE 50 PERCENT INHIBITION OF THE TEST PLANT

	Herbicide							
Adsorbent	CIPC	Tri-fluralin	2,4-D	Di-phenamid	DCPA	DNBP	Amiben	Paraquat
Muck soil	0.78	0.64	0.13	1.4	10.5	37	6.8	31.0
Bentonite Clay	0.45	0.58	0.12	1.4	10.5	34	8.3	81.0
Control (no adsorbent)	0.26	0.14	0.12	1.4	10.5	30	6.8	21.0

Source: Coffey, D.L., and Warren, G.F., 1969. (See Copyright Notice)

Status of Technology

Studies have been conducted at the laboratory stage showing immobilization of pesticides by clays.

Ease of Application

The rate of application (mass per volume of soil) is determined in short-term treatability studies. Clay is applied to the soil surface and thoroughly incorporated through the depth of contamination. Runoff and runon controls may be appropriate if erosion or drainage problems occur. This technology is easy to apply using traditional equipment and methods. However, if the site is not trafficable, it might be difficult to apply.

Potential Achievable Level of Treatment

For certain cationic compounds, the level of treatment achievable is high. As mentioned earlier, other ions present in the waste mixture could effectively reduce the immobilization expected.

Reliability of Method

The interactions of ions in the soil system are very complex. This technology is reliable in that the addition of clay to a soil is likely to cause immobilization of some cations. However, the effectiveness may not be as high as anticipated from theory or tests in the laboratory.

Secondary Impacts

Clay addition may affect the chemical, physical, and biological properties of natural soil. The extent and type of effects are dependent on the characteristics of both native soil and added clay. Tillage will increase susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are necessary to incorporate the clay into the soil.

Information Requirements

- characterization and concentration of wastes, primarily ionic forms present;
- depth, profile, and areal distribution of contamination;
- cationic exchange capacity of clay;
- soil pH;
- selectivity of clay for cations in waste;
- competing, naturally occurring ions at site;
- trafficability of soil and site.

Sources of Information

Brady, N.C., 1974; Coffey, D.L., and Warren, G.F., 1969; Weber, J.B., et al., 1965; Bailey, G.W., et al., 1968; Bonazountas, M., and Wagner, J., 1981.

3.3.2.2 Addition of Synthetic Resins

Description

Synthetic resins consist of a network of hydrocarbon radicals to which ionic functional groups are attached. These hydrocarbon molecules are cross-linked in a three dimensional arrangement, rendering the resin insoluble. The cross-linking of these molecules affects the pore structure of the resin. Ions penetrate these pores in order to be exchanged. Hence, the appropriate resin allows the exclusion of a given size of ions. Synthetic resins can be: 1) those carrying exchangeable cations (acidic), and 2) those carrying exchangeable anions (basic). The advantage of synthetic resins over activated carbon is that they are effective in immobilizing ionic compounds. Despite the high cost and lower sorption capacity of synthetic resins compared with activated carbon, use of synthetic resins is attractive because they can be made selective for specific compounds. The availability and cost of resins do limit their use in large-scale situations like those in hazardous waste sites.

Competition from ionic species found naturally in soil is a problem, decreasing the effectiveness of synthetic resins in the real world.

Wastes Amenable to Treatment

Both organic and inorganics are amenable to treatment with synthetic resins. Cations and anions can be immobilized on synthetic resins with the right choice of resins.

Status of Technology

Synthetic resins (cationic exchange resin, e.g., Chelex 100, and anionic exchange resin, e.g., Dowex 1-X8) have been shown to reduce phytotoxicity of pesticides in the laboratory. Synthetic resins have been effective in removing ionic compounds such as paraquat, DNBP, 2,4-D and amiben from solution.

Ease of Application

The rate of application (mass per volume of soil) should be determined in short-term treatability studies. The resin is applied to the soil surface and thoroughly incorporated through the depth of contamination. Runoff and runon controls may have to be installed to prevent erosion and drainage into the site. This technology should be easy to apply if the depth of contamination is relatively shallow and the site is trafficable.

Potential Achievable Level of Treatment

The achievable treatment level is variably dependent on resin characteristics and competing, naturally occurring ions in the soil.

Reliability of Method

The long-term desorption and stability of resins in soil systems is unknown at the present time. This increases the risk of this technology because of the lack of certainty and the unpredictability of the ion-exchange capacity for a particular ion in natural soils.

Secondary Impacts

Immobilization of organics by synthetic resins may adversely affect rates of biodegradation. Tillage increases the susceptibility of a site to water and wind erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are necessary to apply resins into the soil.

Information Requirements

- characterization and concentration of waste, primarily ionic forms present;
- depth, profile, and areal distribution of contamination;
- ion exchange capacity of synthetic resin;
- soil pH;
- selective characteristics for specific ions present at site;
- trafficability of soil and site.

3.3.2.3. Addition of Zeolites

Description

Molecular sieve zeolites are crystalline, hydrated aluminosilicates with chemical formulae such as $Na_2Al_2Si_4O_{12}$. Ion exchange selectivities in zeolite do not follow the typical rules and patterns exhibited by other inorganic or organic ion exchangers. Zeolites provide certain combinations of selectivity, capacity, and stability characteristics superior to the more common organic and inorganic cation exchangers. Breck (1974) presents detailed information on the properties of zeolites.

Zeolites are highly selective for particular metals. Clinoptilolite and mordenite both show selective sorption of heavy metals (Sherman, 1978):

• Clinoptilolite	$Cu \leq Zn \leq Cd << Pb$
• Mordenite	$Ni < Zn$; and $Co < Cu < Mn$

The maximum theoretical cation exchange capacity for these two zeolites is 2.6 m.e./g. Zeolites have been used to soften water.

Zeolites are stable over a wide alkaline pH range (6-12) and do not biologically degrade. The chief restriction in the use of zeolite ion exchangers is their limited acid resistance. Most zeolite ion exchangers should not be employed below about pH 4-5. At lower pH's, the zeolite will itself degrade. Because of this, it would be recommended that zeolites be used only in alkaline soils or limed soils (pH greater than 6).

As with all cation exchangers, sorption of metals by zeolite is affected by 1) pH, 2) competing cations, 3) choice of solvent, 4) presence of complexing agents, 5) solution ionic strength, and 6) type of anions present. The effect of these variables upon the overall ion exchange performance of zeolites is generally less complex and more predictable than with resin exchangers.

The lack of data, both from laboratory and field studies, on the use of zeolites for metal clean-up in soils makes it difficult to comment on possible undesirable factors that may be involved. Research is needed on potential long-term immobilization.

Wastes Amenable to Treatment

Zeolites can be used to immobilize wastes containing heavy metals.

Status of Technology

This technology is conceptual for immobilization of heavy metals in soil systems. It has been used in agricultural applications for retention of ammonium and potassium. Research is needed to investigate the long-term potential for metal immobilization, although it is effective for removing heavy metals (especially cadmium, copper, lead, and zinc) from wastewater.

Ease of Application

Liming might be necessary to increase the pH to greater than 6. Thorough mixing is required for maximum waste/zeolite contact. This technology may be easy or difficult to apply depending on the trafficability of the site and the depth of contamination.

Practical Achievable Level of Treatment

Zeolites have been found to be effective for removing heavy metals (especially Cd, Cu, Pb, and Zn) from wastewater. They look promising for use in soils, but research is required to investigate the long-term potential for metal immobilization.

Reliability of Method

There are a lot of uncertainties associated with this method. At present, its reliability is unknown.

Secondary Impacts

Tillage would increase the susceptibility of the site to wind and water erosion.

Equipment and Exogenous Reagents

The equipment needed are power implements, tillers, and applicators. Zeolites and liming material are also needed.

Information Requirements

- characterization and concentration of waste, primarily ionic forms present;
- depth, profile, and areal distribution of contamination;
- ion exchange capacity and selectivity for metals at site;
- competing naturally occurring ions at site;
- soil pH;
- trafficability of soil and site.

Sources of Information

Breck, 1974; Sherman, 1978; Coffey, D.L., and Warren, G.F., 1969; Weber, J.B., et al., 1965.

TABLE 3-9. SOLUBILITY PRODUCT CONSTANTS FOR METAL SULFIDES

Substance	Equilibrium	Solubility Product Constants
Sulfides		
Cadmium Sulfide	$CdS=Cd^{++}+S$	6×10^{-27}
Cobalt Sulfide	$CoS=Co^{++}+S$	5×10^{-22}
Cupric Sulfide	$CuS=Cu^{++}+S$	4×10^{-36}
Ferrous Sulfide	$FeS=Fe^{++}+S$	4×10^{-17}
Lead Sulfide	$PbS=Pb^{++}+S$	4×10^{-26}
Manganous Sulfide	$MnS=Mn^{++}+S$	8×10^{-14}
Mercuric Sulfide	$HgS=Hg^{++}+S$	1×10^{-50}
Nickelous Sulfide	$NiS=Ni^{++}+S$	1×10^{-22}
Silver Sulfide	$Ag_2S=2Ag^{+}+S$	1×10^{-50}
Zinc Sulfide	$ZnS=Zn^{++}+S$	1×10^{-20}

Source: Overcash, M.R., and Pal, D., 1979.
(See Copyright Notice)

3.3.3 Precipitation

Another immobilization technology for metals in soils is precipitation. Theoretically, precipitation occurs when the solubility product of the ions forming the precipitate is exceeded in the solution. Metals may be precipitated as sulfides, carbonates, phosphates, and hydroxides. We will discuss sulfides separately from the rest because the method for precipitating sulfides is different from that for precipitating the others.

3.3.3.1 Precipitation as Sulfides

Description

Heavy metals will react with sulfide ions to form insoluble metal sulfides (Table 3-9). These metal sulfides have very low solubilities, even at acidic pH values. The extent of metal sulfide precipitation is a function of 1) pH, 2) type of metal, 3) sulfide content, and 4) interfering ions. A high salt content of the waste will reduce the theoretical extent of precipitation.

With divalent heavy metals the important metal-sulfide reactions are:

$$H_2S \rightleftharpoons H^+ + HS^- \qquad (3\text{-}5)$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad (3\text{-}6)$$

$$Me^{2+} + S^{2-} \rightleftharpoons MeS \qquad (3\text{-}7)$$

The solubilities of metal sulfides decrease with increasing pH (arsenic is an exception, precipitating only at pH <5). With sulfide precipitation, a residual concentration less than 0.1 mg/l metal (for Cd, Cu, Pb, and Zn) can be achieved at $4 \leq pH \leq 12$. Therefore, a single pH level may be used to remove several heavy metals.

Metal sulfides are the least soluble of the metal compounds likely to form in the soil system. Competition from other anion species present would be negligible. The high stability of metal sulfides makes it possible to precipitate metals even in the presence of organic liquids such as chelating agents.

The kinetic aspects of dissolution and precipitation reactions involving heavy metals in the soil matrix have not been studied in detail. Therefore, the time required for maximum precipitation is not known.

Some heavy metals will form soluble sulfide complexes: ZnS_2^{2-}, HgS_2^{2-}, HgS_2H^-, AgS^-, and $As_2S_2^{2-}$. The complexed metal may be more mobile than the free-metal ion. Controlled additions of sulfide by accurate control of pH or sulfide concentration may help prevent the formation of these complexes.

Wastewater treatments have employed several effective sources of sulfide. The sodium salts of sulfide (Na_2S or NaHS) are highly soluble, so that concentrated solutions of sulfide can be prepared. However, addition of Na may have adverse effects on soil physical properties. Calcium sulfide (CaS) has been used, but must be prepared as a slurry because of its low solubility. Iron sulfide (FeS) can additionally reduce Cr^{6+} to Cr^{3+} but, because of its very low solubility, it would not be of practical use in soils as a source of sulfide.

Diking the site, adding gypsum and organic matter, and then flooding the site will provide an anaerobic environment for the reduction of SO_4^{2-} to S^{2-}. This process could be used to provide sulfide for precipitation in soils having sufficiently high sulfate concentrations. However, the possibility of leaching other hazardous constituents must be investigated.

Sulfide precipitates in a natural soil system may be an important mechanism for regulating the solution concentration of heavy metals under reduced conditions only. Sulfides will be oxidized to form soluble metal sulfates under aerobic soil conditions. However, there is no published literature discussing the use of sulfides for reclaiming soils contaminated with metals.

Wastes Amenable to Treatment

Inorganic wastes containing heavy metals, particularly metals with highly insoluble sulfides like copper, cadmium, lead, mercury, and zinc.

Status of Technology

This technology has been used in the field to treat river water and wastewaters. On the laboratory scale, there have been additional studies with wastewater. The treatment of soils by precipitation of sulfides is purely conceptual at the present time.

Ease of Application

Theoretically, one mole of sulfide reacts with one mole of divalent metal. At a waste site, metals are encountered as compounds with various anions. Excess sulfide must be added to ensure that the precipitation is as complete as possible. Calcium sulfide may be applied as a slurry and incorporated. Sodium sulfide may be applied in an irrigation system or with sprayers. The soil must be maintained at reduced conditions. Otherwise, the oxidation of precipitated sulfides to more soluble sulfate compounds may occur under aerobic soil conditions. Runon and runoff controls may have to be installed depending on whether the site has been tilled.

Potential Achievable Level of Treatment

Excellent treatment of wastewaters containing copper, cadmium, lead, mercury, and zinc has been obtained for $4 \leq pH \leq 12$. This technology may prove promising for soil systems, with appropriate soil conditions and careful management.

Reliability of Method

If the precipitated sulfides are subjected to aerobic conditions for long periods of time, they may be oxidized to the more soluble sulfates and be leached from the soil into groundwater. Also, if the pH is lowered, the metals will dissolve, releasing hydrogen sulfide. The soil conditions have to be maintained carefully if the metals are to remain as immobile precipitates.

Secondary Impacts

The use of sodium sulfide salts may affect soil permeability. However, soils low in clays and native sodium may be conducive to sodium sulfide treatments without adverse effects. Incomplete sulfide precipitation under reducing conditions may result in leaching of nonprecipitated metals and other soluble constituents, and the formation of volatile toxic metal compounds.

Hydrogen sulfide, a poisonous flammable gas with an offensive odor, may be formed in the precipitation treatment. However, Bhattacharyya et al. (1981) found no formation of H_2S gas during sulfide precipitation reactions. They attributed this to the high reactivity of sulfides and metals. Pillie et al. (1975) noted that the use of a small amount of NaOH prevented the evolution of H_2S gas. The rate of formation of metal-sulfide precipitates in soils may be slow in comparison with the rate in water. The likelihood of the evolution of H_2S will increase as the reactivity of sulfides and metals decrease. Hydrogen sulfide is neutralized in alkaline soils.

A favorable secondary impact may be a reduction of selenium and chromium as a result of precipitating under reducing conditions.

Equipment and Exogenous Reagents

If calcium sulfide is used as the source of sulfide, power implements, tillers, and an applicator for applying slurries are required. Otherwise, if sodium sulfide is used in solution, sprayers or sprinklers may be used.

Information Requirements

- characterization and concentration of metals in waste, primarily heavy metals;
- depth, profile, and areal distribution of contamination;
- soil pH;
- soil oxygen content;
- solubility of metal sulfide(s);
- oxidation/reduction (redox) potential of waste constituents at site;
- trafficability of soil and site;
- susceptibility of soil permeability to change by addition of sodium.
- hydraulic conductivity of soil

Sources of Information

Bhattacharyya, D., et al., 1981; Pillie, R.J., et al., 1975; Weast, R.C., 1983; King, 1981; Overcash, M.R., and Pal, D., 1979.

3.3.3.2 Precipitation as Carbonates, Phosphates, and Hydroxides

Description

Theoretically, many metals will form insoluble compounds with carbonates, phosphates, and hydroxides. Table 3-10 lists the solubility product constants for these compounds.

TABLE 3-10. SOLUBILITY PRODUCT CONSTANTS FOR METAL CARBONATES, PHOSPHATES, AND HYDROXIDES

Substance	Equilibrium	Solubility Product Constants
Carbonates		
Barium carbonate	$BaCO_3 = Ba^{++} + CO_3^{--}$	1.6×10^{-9}
Cadmium carbonate	$CdCO_3 = Cd^{++} + CO_3^{--}$	5.2×10^{-12}
Calcium carbonate	$CaCO_3 = Ca^{++} + CO_3^{--}$	6.9×10^{-9}
Cobalt carbonate	$CoCO_3 = Co^{++} + CO_3^{--}$	8×10^{-13}
Cupric carbonate	$CuCO_3 = Cu^{++} + CO_3^{--}$	2.5×10^{-10}
Lead carbonate	$PbCO_3 = Pb^{++} + CO_3^{--}$	1.5×10^{-13}
Magnesium carbonate	$MgCO_3 = Mg^{++} + CO_3^{--}$	4×10^{-5}
Manganous carbonate	$MnCO_3 = Mn^{++} + CO_3^{--}$	9×10^{-11}
Nickelous carbonate	$NiCO_3 = Ni^{++} + CO_3^{--}$	1.4×10^{-7}
Silver carbonate	$Ag_2CO_3 = 2Ag^{+} + CO_3^{--}$	8.2×10^{-12}
Strontium carbonate	$SrCO_3 = Sr^{++} + CO_3^{--}$	7×10^{-10}
Zinc carbonate	$ZnCO_3 = Zn^{++} + CO_3^{--}$	2×10^{-10}
Phosphates		
Variscite	$Al(H_2PO_4)(OH)_2 = Al^{3+} + H_2PO_4^{-} + 2OH^{-}$	3×10^{-31}
Strengite	$Fe(H_4PO_4)(OH)_2 = Fe^{3+} + H_2PO_4^{-} + 2OH^{-}$	1×10^{-35}
Octocalcium phosphate	$Ca_4H(PO_4)_3 = 4Ca^{2+} + H^{+} + 3PO_4^{3-}$	1×10^{-47}
Fluorapatite	$Ca_{10}(PO_4)_6(FH)_2 = 10Ca^{2+} + 6PO_4^{3-} + 2F^{-}$	4×10^{-119}
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2 = 10Ca^{2+} + 6PO_4^{3-} + 2OH^{-}$	2×10^{-114}
Hydroxides		
Aluminum hydroxide	$Al(OH)_3 = Al^{+++} + 3(OH)^{-}$	5×10^{-33}
Cadmium hydroxide	$Cd(OH)_2 = Cd^{++} + 2(OH)^{-}$	2.0×10^{-14}
Chromic hydroxide	$Cr(OH)_3 = Cr^{+++} + 3(OH)^{-}$	7×10^{-31}
Cobaltous hydroxide	$Co(OH)_2 = Co^{++} + 2(OH)^{-}$	2.5×10^{-16}
Cupric hydroxide	$Cu(OH)_2 = Cu^{++} + 2(OH)^{-}$	1.6×10^{-19}
Ferric hydroxide	$Fe(OH)_3 = Fe^{+++} + 3(OH)^{-}$	6×10^{-38}
Ferrous hydroxide	$Fe(OH)_2 = Fe^{++} + 2(OH)^{-}$	2×10^{-15}
Lead hydroxide	$Pb(OH)_2 = Pb^{++} + 2(OH)^{-}$	4×10^{-15}
Magnesium hydroxide	$Mg(OH)_2 = Mg^{++} + 2(OH)^{-}$	8.9×10^{-12}
Manganese hydroxide	$Mn(OH)_2 = Mn^{++} + 2(OH)^{-}$	2×10^{-13}
Mercuric hydroxide	$HgO + H_2O = Hg^{++} + 2(OH)^{-}$	3×10^{-26}
Nickel hydroxide	$Ni(OH)_2 = Ni^{++} + 2(OH)^{-}$	0.6×10^{-16}
Zinc hydroxide	$Zn(OH)_2 = Zn^{++} + 2(OH)^{-}$	5×10^{-17}

Source: Overcash, M.R., and Pal, D., 1979. (See Copyright Notice)

Santillan-Medrano and Jurinak (1975) obtained experimental data from soil column studies using both Pb and Cd. Their data showed that for the calcareous Nibley soil: 1) the solubility of Pb decreases with increasing soil pH, which is the usual trend for most heavy metals, 2) lead phosphate compounds could be regulating the activity of Pb^{2+} ion in solution, and 3) mixed compound precipitation cannot be precluded between pH 7.5-8.0 because of the convergence of the solubility isotherms for $PbCO_3$, $Pb(OH)_2$, $Pb_3(PO_4)_2$ and $Pb_5(PO_4)_3Cl$. Similar results were seen for the solubility of Cd in Nibley soil. However, the solubility of Cd is considerably higher than Pb at any pH, and at high pH values the soil solution is undersaturated with respect to the compounds considered. This research showed that precipitation reactions involving native soil carbonates, hydroxides, and phosphates are important in regulating solution concentrations of metals added to the soil.

McBride (1980) concluded that calcite serves as a site for chemisorption of Cd^{2+} at low levels of Cd additions, while $CdCO_3$ precipitation occurs at higher Cd concentrations. Carbonate surfaces are known to chemisorb other heavy metals such as Zn^{2+} (Jurinak and Bauer, 1956) and Mn^{2+} (McBride, 1979), providing a mechanism of metal retention that can lower the solution activity below that predicted by the solubility product of the least soluble pure mineral phase. McBride (1980) found that the initial chemisorption of Cd^{2+} on calcite was very rapid, while $CdCO_3$ precipitation of higher Cd^{2+} concentrations was slow.

Artiole and Fuller (1979) tested the effectiveness of using a limestone barrier as a landfill liner to retard the migration rate of metals. The test was conducted in a laboratory column study using a leachate generated from municipal solid waste. The use of a limestone barrier increased the retention of the metals studied (Be, Cd, Fe, Ni, Zn and Cr) as is shown in Table 3-11.

TABLE 3-11. RELATIVE EFFECT OF CRUSHED LIMESTONE LINER PLACED OVER SOIL ON THE PREVENTION OF HEAVY METALS IN MUNICIPAL SOLID WASTE LANDFILL LEACHATE FROM MIGRATING

	Pore Volume Displacement to Achieve the Same C/C_o[a]											
	With Limestone Layer With Soil						No Limestone Layer, Soil Only					
Element	1[b]	2	3	4	5	6	1	2	3	4	5	6
Be	30	29	35	30	30	25	10	16	15	15	18	10
Cd	30	35	40	38	35	35	16	18	28	15	18	6
Cr (pH 2.5)	35	52	85	88	86	35	10	15	5	10	10	6
Cr (pH 4.0)	28	49	125	144	111	109	2	21	39	25	17	15
Fe	31	31	35	36	30	25	21	26	10	25	10	10
Ni	40	35	30	35	28	24	20	15	11	15	7	10
Zn	30	25	30	32	25	30	10	11	15	18	12	16

a. Determination used in column studies, where C = concentration of effluent, C_o = concentration of influent. The higher the pore volume displacement, the greater the volume that was passed through the column to achieve the same C/C_o, and therefore the greater the compound was retained in the column.

b.

Soil Characteristics	pH	Texture
1. Davidson	6.2	clay
2. Ava	4.5	silty-clay-loam
3. Anthony	7.7	sandy-loam
4. Mohave	7.3	sandy-loam
5. Kalkaska	4.7	sand
6. Wagram	4.2	loamy-sand

Source: Artiole, J., and Fuller, W.H., 1979. (See Copyright Notice)

TABLE 3-12. SOME PROBABLE BIVALENT METAL COMPLEXES WITH INORGANIC LIGANDS IN SOIL SOLUTIONS

OH	Cl	SO_4	CO_3	PO_4
MOH^+	MCl^+	$MHSO_4^+$	$MHCO_3^+$	$MH_2PO_4^+$
$M(OH)_2^0$	MCl_2^0	MSO_4^0	$M(HCO_3)_2^0$	$MHPO_4^0$
$M(OH)_3^-$	MCl_3^-	$M(SO_4)_2^{2-}$	MCO_3^0	MPO_4^-
$M(OH)_4^{2-}$	MCl_4^{2-}		$M(CO_3)_2^{2-}$	

Source: Mattigod, S.W., et al., 1981. (See Copyright Notice)

For maximum treatment effectiveness, soil pH must be maintained over time. In a calcareous soil this should not pose any problems. In an acid soil, however, the pH of the soil must be adjusted to a pH greater than 6 and maintained with continued liming of the soil.

In determining the amount of $CaCO_3$ to be added to increase the pH and thus precipitate the metals present, consideration must be given to the lime requirement of the soil. The lime requirement calculation indicates the amount of lime required to reach a predetermined pH. Lime in excess of this amount will also provide an adsorbing surface for a number of heavy metals.

When applying relatively soluble treble superphosphate fertilizer $[Ca(H_2PO_4)_2]$ to the soil to precipitate metals as phosphates, consideration must be given to the competitive interaction for phosphate of the soil constituents. In acid soils this would be iron and aluminum compounds, whereas excess calcium existing in alkaline soils is competitive for the phosphate anion.

Maximum insolubility of metal-hydroxides occurs at different pH values for each heavy metal. Selection of an optimum pH for all metals that may be involved in a treatment process is not possible. Because of this, Kim (1980) and Bhattacharyya et al. (1983) recommended the use of sulfide in treating wastewater for metals. This same pH-dependency on optimum precipitation is also true for carbonates and phosphates.

Heavy metals may also form soluble phosphate, carbonate, and hydroxide complexes (Table 3-12). These complexed metals may be more mobile than the free metal ion. Controlled additions of the anions and optimizing pH for precipitation versus complex-formation may help prevent the formation of these complexes.

The kinetic aspects of dissolution and precipitation reactions involving heavy metals in the soil matrix have not been studied in any detail. Also, high salt content of any accompanying waste as well as chelating agents and other competing reactions may reduce performance of these treatments.

Wastes Amenable to Treatment

Inorganic wastes containing metals, particularly heavy metals, are amenable to this treatment.

Status of Technology

Hydroxide precipitation has been used effectively in wastewater treatment of metals. The use of limestone as a barrier to retard the migration of heavy metals from landfill leachate has been successfully demonstrated in the laboratory.

Ease of Application

Hydroxide salts are highly corrosive and their direct application to soil is not recommended. Hydroxide ions are formed when a soil is treated with liming materials, and they are available for hydroxide-metal precipitation reactions. After adjusting soil pH to the optimum pH for precipitation, theoretically, for divalent metals, one mole of carbonate (two moles of hydroxide) reacts with one mole of metal. However, at a hazardous waste site, the complexity of the soil matrix and wastes make simple estimates impossible and excess carbonate or phosphate should be used. Treble superphosphate fertilizer, which is relatively soluble, may be used to provide phosphate ions.

Limestone and treble superphosphate are both easy to handle agricultural chemicals. No special equipment or safety considerations are necessary. Soil pH must be maintained at a value conducive to maximum insolubility of the specific metal precipitate. Thorough mixing is required for maximum waste and reagent contact. Controls to prevent runon and runoff may be necessary because tillage will increase the susceptibility of the site to erosion.

Potential Achievable Level of Treatment

Insoluble metal compounds of phosphate, carbonate, and hydroxide are known to participate in regulating solution concentrations of metals in natural soil systems. Little, however, is known about using precipitation as a means of treating metals in soils. The kinetics of metals precipitation in soils may limit the effectiveness of this treatment. Also, high salt content of waste, as well as any chelating agents and other competing reactions, may reduce the performance of this treatment.

Reliability of Method

Because precipitation reactions are pH-dependent, it is necessary to maintain the pH of the soil system at high levels to prevent dissolution of the precipitates and subsequent leaching. Reliming is necessary at intervals.

Secondary Impacts

If arsenic is present in the system, the use of phosphate may cause the release of arsenate to the soil solution. Heavy metals may form soluble phosphate, carbonate, and hydroxide complexes which are more mobile than the free metal ion. Tillage will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements, tillers and applicators are necessary. Calcium carbonate and treble superphosphate fertilizer are required as the precipitating agents.

Information Requirements

- characterization and concentration of metals in waste, primarily heavy metals;
- depth, profile, and areal distribution of contamination;
- soil pH;
- oxidation/reduction (redox) potential of waste constituents at site;
- iron and aluminum compounds, calcium (phosphate fixation capacity);
- soil arsenic (oxidation state and concentration);
- solubility of precipitates (carbonates, phosphates, and hydroxides);
- trafficability of soil and site.

TABLE 3-13. OXIDATION REACTIVITY FOR ORGANIC CHEMICAL CLASSES

Reactivity		
High	**Moderate**	**Low**
Phenols	Alcohols	Halogenated hydrocarbons
Aldehydes	Alkyl-substituted aromatics	Saturated aliphatic compounds
Aromatic amines	Nitro-substituted aromatics	Benzene
Certain organic sulfur compounds	Unsaturated alkyl groups	Chlorinated insecticides
	Aliphatic ketones	
	Aliphatic acids	
	Aliphatic esters	
	Aliphatic amines	

Source: JRB, 1982.

Sources of Information

Santillan-Medrano, J., and Jurinak, J.J., 1975; Overcash, M.R., and Pal. D., 1979; McBride, M.B., 1979, 1980; Jurinak, J.J., and Bauer, N., 1956; Antiole, J., and Fuller, W.H., 1979; Kim, B.E., 1981; Bhattacharyya, D., et al., 1983; Mattigod et al., 1981; Dept. of Army, 1982.

3.4 DEGRADATION

3.4.1 Chemical

Chemicals naturally undergo reactions in soil that may transform them into more or less toxic products, or which may increase or decrease their mobility within the soil system. Chemical treatment of contaminated soils entails the reaction of pollutants with reagents, resulting in products which are less toxic, or which become immobilized in the soil column. These reactions may be classified as oxidation reactions, reduction reactions, and polymerization reactions.

3.4.1.1 Oxidation

Chemical oxidation is a process in which the oxidation state of an atom is increased. This is accomplished by removal of electrons or addition of oxygen to the atom. Chemical oxidation represents a significant treatment process in soil systems. As a result of oxidation, a substance may be transformed, degraded, and/or immobilized in soil. Oxidation reactions within the soil matrix may occur through management of the natural processes in a soil, or through addition of an oxidizing agent to the soil-waste complex. Certain compounds are more oxidizable in soils than others. General oxidation reactivity for organic chemical classes is summarized in Table 3-13.

The following discussion is primarily concerned with the oxidation of organics. Oxidation of heavy metals is not usually effective as a treatment method because the higher the oxidation state, the more mobile the heavy metal tends to be. Arsenic is an exception. It is discussed here rather than separately because there is very little information on its oxidation.

Arsenate (As(V)) is less toxic and forms less soluble compounds than arsenite (As(III)). Treatment, therefore, consists of oxidizing As(III) to As(V) followed by the addition of 1:1 ferrous sulfate to precipitate ferric arsenate

(FeAsO4), a highly insoluble compound. Aluminum sulfate, zinc sulfate, organic matter, or lime can also be used as a means of fixing As(V). Volatile arsines are formed under anaerobic conditions which, therefore, must be avoided. There is a lack of research dealing with methods for oxidation of arsenic. Aeration may be adequate. Also, there is presently no analytical technique for distinguishing between As(III) and As(V).

3.4.1.1.1 Soil Catalyzed Reactions

Description

Iron, aluminum, trace metals within layer silicates, and adsorbed oxygen have been identified as catalysts promoting free-radical oxidation of constituents in soil systems (Page, 1941; Solomon, 1968; Theng, 1974; Furukawa and Brindley, 1973; and Hirschler, 1966). General characteristics of the organic chemicals likely to undergo oxidation include: 1) aromaticity, 2) fused ring structures, 3) extensive conjugation, and 4) ring substituent fragments.

For oxidation to occur in soil systems, the redox potential of the solid phase must be greater than that of the organic chemical contaminant. Therefore, the half-cell potentials, $E_{1/2}$, of chemical contaminants need to be below the redox potential, 0.8V of a well oxidized soil (Dragun and Baker, 1979).

Another characteristic that is significant with respect to soil-catalyzed oxidation is the solubility of the organic contaminant. The oxidation reaction site is the hydrophilic clay mineral surface, and sorption to the surface precedes soil-catalyzed oxidation. Therefore, more water-soluble compounds should be more readily oxidized in clay-catalyzed systems.

Soil water content (degree of saturation) may also play a very important role in controlling, and therefore managing, soil-catalyzed oxidation. Greater oxidation of chemical contaminants is expected in less saturated soils (Dragun and Helling, 1982). Therefore the technique for immobilization by control of soil moisture is completely compatible with this treatment technique.

Techniques for immobilization by control of soil moisture or by incorporation or addition of uncontaminated soil should not only augment sorption, but they should also augment clay catalyzed reactions in the soil B-horizon where the clay fraction of soil is predominant. Thus a physical-chemical and biological treatment system may be achieved in a layered system through the soil where sorption of hydrophobic constituents occurs in the upper soil layers, or where organic matter content is high, and chemical reactions for hydrophilic constituents occur in lower soil layers where the clay fraction predominates. Biological activity may be expected to increase the extent of degradation of constituents as the retention time of constituents is increased through sorption.

Wastes Amenable to Treatment

Organic wastes which are water-soluble and have half-cell potentials below the redox potential of a well oxidized soil are amenable to this treatment. Table 3-14 lists chemicals which do not undergo free-radical oxidation at soil and clay surfaces. Included in this group of chemicals is the aliphatic class of compounds.

Status of Technology

Soil-catalyzed oxidation reactions have been verified in the field for several chemical classes, including S-triazines and organo-phosphate compounds. Some other compounds have been verified in the laboratory. Otherwise, this technology is at the conceptual stage.

Ease of Application

If required, clay may be applied to the soil surface and thoroughly incorporated through the depth of contamination. The site may require installation of drainage systems to reduce soil moisture. Tillage may be used to dry and

TABLE 3-14. SOME CHEMICALS THAT DO NOT OXIDIZE AT SOIL AND CLAY SURFACES

Chemical Name
Acetamide
Acetone, anisilidene-
-, dianisilidene-
-, dicinnamylidene-
-, dibenzylidene-
β-Carotene
Cyclohexylamine
Monoethanolamine
Triethylamine

Source: Dragun, J., and Helling, C.S., 1982.

aerate the soil. Increasing soil temperatures may enhance soil drying and increase the rate of reaction. This treatment technology requires aerobic soil conditions to be maintained which may be easy or difficult, depending on the site and the depth of contamination as it affects the ability to incorporate clays.

Potential Achievable Level of Treatment

The level of treatment achievable is variable, depending on the oxidation potential of the waste constituents and the aeration of the soil.

Reliability of Method

The chemical degradation of a compound does not guarantee less mobile or less toxic products. Care must be taken that oxidation of the waste will not produce substances more problematic than the parent compounds in the waste.

Secondary Impacts

Decreased soil moisture may result in possible retardation in microbial activity or increased volatilization of volatile waste constituents. Volatilization may present a public health hazard, but also may reduce toxic concentrations to soil micro-organisms. Toxic concentrations may also be reduced by attenuation with the added soil. Other clay-catalyzed degradation may be enhanced by this treatment. Tillage will increase the susceptibility of the soil to erosion.

Equipment and Exogenous Reagents

Equipment to set up a drainage system may be necessary, together with applicators and tillers to incorporate the clay.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- potential for oxidation of waste constituents (half-potentials, $E_{1/2}$);
- oxidation products (particularly hazardous products);
- solubility of organics;
- depth, profile, and areal distribution of contamination;
- soil moisture;
- soil type and profile;
- catalysts for oxidation present in soil;
- trafficability of soil and site.

TABLE 3-15. RELATIVE OXIDATION POWER OF OXIDIZING SPECIES

Species	Oxidation Potential Volts	Relative Oxidation Power
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radicals	1.70	1.25
Hypochlorous acid	1.49	1.10
Chlorine	1.36	1.00

Source: Rice, 1981. (See Copyright Notice)

Sources of Information

Page, 1941; Solomon, 1968; Theng, B.K.G., Furakawa, T., and Brindley, 1973; Hirschler, 1966; Dragun and Baker, 1979; Dragun and Helling, 1982.

3.4.1.1.2 Addition of Oxidizing Agents

Description

Oxidizing agents may be utilized to degrade organic constituents in soil systems. Oxidation reactions are usually limited in application due to their substrate specificity and pH dependence. Two powerful oxidizing agents considered for in-place treatment include ozone and hydrogen peroxide. The relative oxidizing ability of these chemicals, compared with other well known oxidants is indicated in Table 3-15. A serious potential limitation to the use of oxidizing agents for soil treatment is the additional consumption of the oxidizing agent(s) by nontarget constituents comprising the soil organic matter.

Ozone is an oxidizing agent that may be used to degrade recalcitrant compounds directly, to create an oxygenated compound without chemical degradation, and/or to increase the dissolved oxygen level in the water for enhancing biological activity. Ozone is a colorless gas characterized by a pungent odor and very high oxidation potential.

The rate of decomposition of ozone is also strongly influenced by pH. Ozone reactions are believed to be of two fundamental types: 1) direct reaction of ozone with the organic compounds, and 2) free radical reaction of ozone, which involves a hydroxyl free-radical intermediate. Direct reaction of ozone with solute achieves the most rapid decomposition of solute. At high pH, the hydroxyl free-radical reactions have been observed to dominate over the direct ozone reactions. Thus the relative rate of ozone reaction can be controlled by adjusting the pH of the medium.

The most efficient and cost-effective uses of ozone in soil system decontamination appear to be in the treatment of contaminated water extracted from contaminated soil systems through recovery wells, and in the stimulation of biological activity in saturated soil (Nagel et al., 1982). If the specific organic constituents present in contaminated soil are relatively biodegradable, ozone treatment may be very effective as an enhancement of biological activity. However, if a large fraction of the matrix is relatively biorefractory, the amount of ozone that will be required to directly treat the waste by chemical destruction will be a direct function of the organic matter present in the solution and in the soil, and will represent a greatly increased cost of treatment. The presence of natural soil organic matter will greatly increase ozone dosage and consumption necessary to treat the target constituents.

Groundwater contaminated with oil products were treated with ozone to reduce dissolved organic carbon (DOC) concentration (Nagel et al., 1982). Dosages of 1 gram ozone per gram dissolved organic carbon resulted in residual water ozone concentration of 0.1 to 0.2 ppm. The treated water was then infiltrated into the aquifer through injection wells. An increase in dissolved oxygen (DO) in the contaminated water was demonstrated. The increase in DO increased microbial activity in the saturated soil zone which stimulated microbial degradation of the organic contaminants. Thus, ozone can be effectively used to treat contaminated water extracted from the soil system and to stimulate biological activity in deeper saturated zones of contaminated soils.

Hydrogen peroxide is an oxidant that has been successfully used in wastewater treatment to degrade compounds that are resistant to biological treatment (recalcitrant). It has also been used to modify the mobility of some metals.

Hydrogen peroxide can react in three major ways:

1) Direct reaction with substrate as shown in Equation 3-8, where the peroxide reacts with silver nitrate to form elemental silver and nitric acid:

$$2AgNO_3 + H_2O_2 \longrightarrow 2Ag + O_2 + 2HNO_3 \tag{3-8}$$

2) Hydrogen peroxide can be degraded by UV light to form hydroxyl free radicals as shown in Equation 3-9:

$$H_2O_2 + \underset{2.537A}{UV} \rightarrow 2OH^- \tag{3-9}$$

3) It can undergo auto-decomposition in the presence of a metal catalyst as in Equation 3-10:

$$6\ H_2O_2 \xrightarrow{\text{Metal}} 6\ H_2O + 3\ O_2 \tag{3-10}$$

Hydrogen peroxide has also been used in conjunction with ozone to degrade compounds which are refractory to either material individually (Nakayama et al., 1979).

Peroxide, as demonstrated in Equations (3-8) and (3-10), can be used to increase oxygen levels in the soil. A previous study (Nagel et al., 1982) has shown an increase in microbial activity and microbial degradation of organic contaminants with increasing oxygen content in soil/groundwater systems.

Hydrogen peroxide is a strong oxidant and, as a result, it is nonselective. If this material is added to the soil, it will react with any oxidizable material present in the soil. This will be a major concern because the concentration of natural organic material in the soils may be lowered, resulting in decrease sorption capacity for some organics.

Thus, the effectiveness of peroxide may be inhibited because it simultaneously increases mobility and decreases possible sorption sites.

Wastes Amenable to Treatment

Organic wastes are amenable to treatment by the addition of oxidizing agents, subject to considerations of the production of more toxic or more mobile oxidation products.

TABLE 3-16. HAZARDOUS PRODUCTS OF OZONE REACTIONS

Parent Compound	Reaction Product	Oxidation of Product with Ozone
Aldrin	Dieldrin	Very slow
Heptachlor	Heptachlor epoxide	Stable to further oxidation
DDT	DDE	—
Parathion	Paraoxon	Nitrophenols, phosphoric acid
Malathion	Malaoxon	—

Source: Utah Water Research Laboratory.

Some hazardous compounds are known to be non-reactive with ozone. Unreactive chemical species are usually characterized by inorganic compounds in which cations and anions are in their highest oxidation state, or organic compounds which are highly halogenated. There are many hazardous chemicals for which no information currently exists concerning their susceptibility to ozone oxidation.

Some general rules concerning chemical destruction of organic constituents include the following:

1) Saturated aliphatic compounds which do not contain easily oxidized functional groups are not readily reactive with ozone. Examples include saturated aliphatic hydrocarbons, aldehydes, and alcohols.

2) For aromatic compounds, reactivity with ozone is a function of the number and type of substituent(s). Generally, substituents which withdraw electrons from the ring deactivate the ring toward ozone. Examples include halogens, nitro, sulfonic acid, carbonyl, and carboxyl groups. Substituents which release electrons activate the ring toward ozone. Examples include alkyl, methoxyl, and hydroxyl.

The following general patterns concerning reactivity with ozone have been identified:

1) phenol, xylene > toluene > benzene
2) pentachlorophenol < dichloro-, trichloro-, tetrachlorophenol

Ozonation of hazardous pesticides may actually be detrimental in many instances. Table 3-16 presents specific examples in which reactions of ozone with parent compounds result in the production of hazardous products, which are often degraded very slowly with ozone.

Hydrogen peroxide has been demonstrated to be effective for oxidizing cyanide, aldehydes, dialkyl sulfides, dithionate, nitrogen compounds, phenols, and sulfur compounds (FMC Corp., 1979).

Peroxide also reacts with many chemical classes with a resultant increase in mobility for the products (JRB, 1982). Table 3-17 shows chemical groups having incompatible reactions with peroxides (i.e., reaction products are more mobile).

Status of Technology

Oxidizing agents are used in wastewater treatment, but there is little experience with their use in terrestrial systems. Hydrogen peroxide is used in septic tank drainfields experiencing failure due to biological clogging.

TABLE 3-17. CHEMICAL GROUPS THAT REACT WITH PEROXIDES TO FORM MORE MOBILE PRODUCTS

Acid chlorides and anhydrides	Cyanides
Acids, mineral, non-oxidizing	Dithio carbamates
Acids, mineral oxidizing	Aldehydes
Acids, organics	Metals and metal compounds
Alcohols and glycols	Phenols and cresols
Alkyl halides	Sulfides, inorganic
Azo, diazo compounds, hydrazine	Chlorinated aromatics/alicycles

Source: Utah Water Research Laboratory.

Ease of Application

The soil should not be disturbed to avoid dilution of contaminants in the soil. The oxidizing agents may be applied in water solutions directly onto the soil surface, injected into the subsurface, or applied through injection wells, depending on the depth and location of contamination. Loading rates can be determined in short-term treatability studies.

Application may be moderate to difficult because oxidizing agents are dangerous to handle and require special treatment. Controls to manage runon and runoff may also be necessary.

Potential Achievable Level of Treatment

The achievable level of treatment is potentially high for wastes susceptible to oxidation, in soils without large quantities of competing oxidizable substances, and for limited areas of contamination.

Reliability of Method

Because ozone and hydrogen peroxide are very strong oxidizers, they are not particularly discriminating in the substances which they will oxidize in the soil. As a result, much of the oxidant will be wasted on oxidizing non-target compounds. Treatment may have to be repeated should initial applications be insufficient, or if the non-target compounds were more susceptible to oxidation than the oxidizable compounds which were problematic at the site.

Secondary Impacts

Oxidizing agents may result in violent reactions with certain classes of compounds (e.g. metals), and may be corrosive to application equipment. Their use may also affect soil hydraulic properties (e.g., infiltration rate), especially in structured soils. Oxidation of soil organic matter may decrease sorption sites for nonoxidizable waste constituents. Oxygenated degradation products are expected to be more polar than the parent compounds and, therefore, potentially more mobile. The chemical reaction may produce a large quantity of potentially mobile constituents in a relatively short period of time, necessitating the installation of recovery wells. The oxygenated products may also be toxic to soil systems, human health, and the environment. Some products may be more refractory than the parent compounds. The use of oxidizing agents may also increase the mobility of some metals. Oxidizing agents may have beneficial effects on microbial degradation processes by adding O_2 to the soil water solution.

Equipment and Exogenous Reagents

Power implements are required. If ozone is used, an ozone generator is necessary. Depending on the application method, an irrigation system, applicators, and/or injection wells may be needed. Exogenous reagents needed are oxidizing agents, ozone or hydrogen peroxide.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- potential for oxidation of waste constituents (half-cell potentials, $E_{1/2}$);
- oxidation products (particularly hazardous products);
- depth, profile, and areal distribution of contamination;
- soil and waste pH;
- other naturally occurring oxidizable substances in soil at site;
- selectivity of oxidizing agent(s) for specific wastes present at site;
- trafficability of soil and site.

Sources of Information

Nagel, G., et al., 1982; Nakayama, S., et al., 1979; FMC Corp., 1979; JRB Inc., 1982; Pringle, Jr., H.W., 1977; Rice, R.G., 1981; Griffin, R.A., and Shimp, N.F., 1978; Metsy, A.A., 1980; Overcash, M.R., and Pal, D., 1979; Woolson, E.A., 1977.

3.4.1.2 Reduction

Chemical reduction is a process in which the oxidation state of an atom is decreased. Reducing agents are electron donors, with reduction accomplished by the addition of electrons to the atom. Reduction of chemicals may occur naturally within the soil system. Certain compounds are more susceptible to reduction than others because they will accept electrons. Addition of reducing agents to soil to degrade reducible compounds can be used as an in-place treatment technology.

Reducing agents and conditions of reduction vary with organics and with metals. The following discussion is divided into organics, chromium, and selenium for ease of organization of the information.

3.4.1.2.1 Organics — Addition of Reducing Agents

Description

Chemical reduction using catalyzed metal powders and sodium borohydride has been shown to degrade toxic organic constituents. Reduction with catalyzed iron, zinc, or aluminum affect treatment through mechanisms including hydrogenolysis, hydroxylation, saturation of aromatic structures, condensation, ring opening, and rearrangements to transform toxic organics to innocuous forms.

The use of catalyzed metal powders has been used successfully for aqueous solutions passed through beds of reactant diluted with an inert solid (Sweeney, 1981). The process may be adaptable to terrestrial application, although this has not been directly demonstrated at this time. The process has been used successfully on the following specific constituents:

hexachlorocyclopentadiene
p-nitrophenol
trichloroethylene
chlorobenzene
kepone

PCBs
chlordane
chlorinated phenoxyacetic acid
di- and tri-nitrophenols
atrazine

Iron powders are preferred for soil systems and are also the most cost-effective and available. Reactions of iron with some organic constituents are as follows:

1) Removal of halogen atom and replacement by hydrogen in halogenated organic species:

$$Fe + H_2O + RCl \rightleftharpoons RH + Fe^{++} + OH^- + Cl^- \qquad (3\text{-}11)$$

An example is the transformation of DDT to DDA.

2. Replacement of a halogen by a hydroxyl group:

$$Fe + 2H_2O + 2RCl \rightleftharpoons 2ROH + Fe^{++} + 2Cl^- + H_2 \qquad (3\text{-}12)$$

3. Saturation of an aromatic structure:

$$Fe + 2H_2O + RCH = CHR \rightleftharpoons RCH2CH2R + Fe^{++} + 2OH^- \qquad (3\text{-}13)$$

An example is the transformation of chlorobenzene to cyclohexanol.

4. Condensation of species:

$$Fe + 2RCl \rightleftharpoons R\text{-}R + 2Cl^- + Fe^{++} \qquad (3\text{-}14)$$

An example is the condensation of DDT to TTTB.

Consumption of metal occurs through the reactions discussed above and also through reactions of the active metal with water:

$$Fe + 2H_2O \rightleftharpoons Fe^{++} + 2OH^- + H_2 \qquad (3\text{-}15)$$

The total consumption of metal from these reactions in aqueous solutions of industrial wastewaters produces 1 to 5 mg/l of metal ($F_e{}^{++}$) in the solution when low toxicant levels are treated.

Organic chemical constituents in soil may also be chemically reduced through the use of sodium borohydride and zinc. These chemicals have been successful for in-place, small-scale field experiments with soils (Staiff et al., 1981). Results of reductive treatment for degradation of paraquat in soil is summarized in Table 3-18. Results indicate that sodium borohydride and powdered Zn/acetic acid combinations accomplished very effective degradation of paraquat in soil and sand media. Toxic products that may be produced as a result of reductive treatment and other by-products were not investigated to any significant extent in this study.

Wastes Amenable to Treatment

Chlorinated organics, unsaturated aromatics and aliphatics, and other organics that are susceptible to reduction will be amenable to treatment by reducing agents.

Status of Technology

Reduction with catalyzed metal powders has been utilized in wastewater treatment systems. Reduction of paraquat with sodium borohydride and powdered zinc has been demonstrated in small-scale field plots.

TABLE 3-18. CHEMICAL REDUCTIVE TREATMENT FOR DEGRADATION OF PARAQUAT IN SOIL

Chemical Treatment	**Paraquat in Soil (ppm)**		
	Initial (1 day)	**4 Months**	**Comment**
None	9,590	6,300	—
$NaBH_4$-soil	None detected	None detected	Violent foaming
$NaBH_4$-sand	None detected	None detected	No foaming
Powdered Zn acetic acid	60	69	Some bubbling

Source: Staiff, D.C., et al., 1981. (See Copyright Notice)

Ease of Application

The soil should not be disturbed prior to treatment to avoid dilution of contaminants in the soil. For metal-catalyzed powders, stoichiometric excess of reductant powder should be applied to the soil surface and mixed with the contaminated soil to achieve maximum contact. For chemical reducing agents, a sodium borohydride-stabilized water solution should be applied to the soil at 50 percent stoichiometric excess. A solution used in a small-scale study contained:

Sodium borohydride	12 ± 0.5%
Sodium hydroxide	42 ± 2%
Water	balance

Iron may be more desirable than zinc or aluminum, since iron is naturally present in most soils. Aluminum is toxic to biological systems and contributes to soil acidity. Soil pH must be maintained at pH 6-8 for maximum treatment effectiveness. Soil water should be controlled at less than saturated conditions (60-80% of field capacity) to provide an aqueous environment for reductive reactions to occur while preventing leaching.

Controls may be necessary for runon and runoff management. Depending on the trafficability of the site and the depth and the extent of contamination, application of this technology may be easy or it may be difficult.

Potential Achievable Level of Treatment

The achievable level of treatment is potentially high for wastes susceptible to reduction, and for limited areas of contamination. The soil must be without large quantities of competing constituents susceptible to reduction, or the level of treatment may be greatly decreased.

Reliability of Treatment

Treatment may have to be repeated if the reducing agents are not sufficient because of high levels of naturally occurring reducible compounds in the soil.

Secondary Impacts

The use of reducing agents may also degrade soil organic matter. The extent of impact on soils is not known at the present time. The products of reduction may present problems with respect to toxicity, mobility, and degradation. Little information is available at the present time. The addition of metals to soil adds to the metal contaminant load.

Iron appears to be the least damaging to the soil system, though iron has a secondary drinking water standard and is of concern with respect to aesthetics. Addition of metals with acetic acid may possibly increase metal mobility by decreasing soil pH. Addition of sodium borohydride may adversely impact soil permeability, depending on the type and content of clay and ionic constituents in the soil solution.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are needed. An irrigation and drainage system is needed to apply the sodium borohydride and to maintain the soil moisture at an optimum level. Reducing agents are necessary.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- potential for reduction of waste constituents;
- reduction products;
- depth, profile, and areal distribution of contamination;
- soil and waste pH;
- soil moisture;
- selectivity of reducing agent(s) for specific wastes present at site;
- trafficability of soil and site.

Sources of Information

Staiff, D.C., 1981; Sweeney, K., 1981.

3.4.1.2.2 Chromium — Addition of Reducing Agents

Description

Hexavalent chromium is highly toxic and highly mobile in soils. Treatment consists of reducing Cr (VI) to Cr (III), which is less toxic and is readily precipitated by hydroxides over a wide pH range. In a study of the relative mobility of metals in soils at pH 5, Cr (III) was found to be the least mobile (Griffin and Shimp, 1978).

Acidification agents (such as sulfur) and reducing agents (such as leaf litter, acid compost or ferrous iron) may serve in the conversion of Cr (VI) to Cr (III) (Grove and Ellis, 1980). Hexavalent chromium itself is a strong oxidizing agent under acidic conditions and, as such, Cr (VI) will be readily reduced to Cr (III), even without the addition of strong reducing agents. After reduction, liming of the soil will precipitate Cr (III) compounds. Precipitation of Cr (III) occurs at pH 4.5-5.5, so little soil pH adjustment is necessary. Caution is required, however, since trivalent chromium can be oxidized to Cr (VI) under conditions prevalent in many soils, e.g., under alkaline and aerobic conditions in the presence of manganese.

Wastes Amenable to Treatment

Wastes containing hexavalent chromium are amenable to this treatment technology.

Status of Technology

Laboratory data support the theory of this treatment method. Treatment of soils has been performed under field conditions.

Ease of Application

Acidification requirements for the particular soil need to be determined. Three moles of ferrous sulfate will reduce one mole of Cr (VI). Excess of this amount will probably be needed to account for other reduction reactions occurring in the soil. The quantity of organic material cannot be predicted from stoichiometric considerations. Liming materials, after the acidification and reducing steps, are applied to raise the pH to greater than 5.

Leaf litter and compost are easily applied to soils by standard agricultural practices, if site/soil trafficability is suitable. Ferrous sulfate may be applied directly to soil or through an irrigation system. Reduction of Cr (VI) must occur under acidic conditions, followed by liming to precipitate Cr (III). Acidification and liming are standard agricultural practices.

Runon and runoff controls may have to be installed to prevent erosion and drainage problems.

Potential Achievable Level of Treatment

The potential achievable level of treatment is high.

Reliability of Method

The pH of the system has to be maintained at greater than 5. Reliming may be necessary at intervals to ensure that the chromium is immobilized in the soil.

Secondary Impacts

Tillage increases the susceptibility of the site to water and wind erosion, and organic materials may have many effects on soil properties, including:

- degree of structure;
- water holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction in soil erosion potential;
- soil temperature.

Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material.

Equipment and Exogenous Reagents

Power implements, tillers, applicators, and an irrigation system are necessary to apply the reducing, acidifying, and liming materials.

Information Requirements

- characterization and concentration of metals, particularly Cr (VI), arsenic, mercury, and other constituents whose treatment requirements may be incompatible;
- depth, profile, and areal distribution of contamination;
- soil pH;
- soil organic matter;
- acidification, reduction, and liming reaction rates;

- trafficability of soil and site.

Sources of Information

Griffin and Shimp, 1978; Grove and Ellis, 1980; Metsy, 1980.

3.4.1.2.3 Selenium — Addition of Reducing Agents

Description

Hexavalent selenium (as selenate (SeO_4^{2-})) is highly mobile in soils. It is the dominant form of selenium in calcareous soils. Elemental selenium and selenite (Se(IV)) are less mobile in soils. Hexavalent selenium can be reduced to Se (IV) or Se° under acid conditions. Reduction of selenium occurs naturally in soils. Elemental selenium is virtually immobile in soils. Se (IV) will participate in sorption and precipitation reactions, but unlike the metals discussed previously, selenite is an anion (SeO_3^{2-}) and its potential leachability will increase with increasing pH. Therefore, at a site that contains selenium as well as other metals, selenium could not be treated if increased pH were required as part of the treatment for the other metals.

Wastes Amenable to Treatment

Wastes containing hexavalent selenium (SeO_4^{2-}) that do not contain significant amounts of other metallic constituents are the most amenable to treatment by this method.

Status of Technology

Studies have been limited to those involving basic chemistry of selenium in soils.

Ease of Application

The soil requires acidification with sulfur or another agricultural acidifying agent to pH 2-3. Acidification requirements for the particular soil need to be determined experimentally. Leaf litter or compost are easily applied to soils by standard agricultural practices, if site trafficability is suitable. Ferrous sulfate may be applied directly to soil or through an irrigation system. Two moles of ferrous sulfate will reduce one mole of Se(VI). Excess of this amount should be added to account for other reduction reactions that may occur in the soil. The quantity of organic material cannot be predicted from stoichiometric considerations.

Runoff and runon controls may be necessary to prevent erosion and drainage problems.

Potential Achievable Level of Treatment

The addition of reducing agents speeds up the natural process of selenium reduction in soils. The potential level of treatment should be high.

Reliability of Method

Once reduction has occurred, the soil must be kept acidic. Reapplication of an acidifying agent may be necessary as required to maintain the pH to between 2 and 3.

Secondary Impacts

Low pH will adversely affect microbial activity and degradation of organic waste constituents. Tillage increases the susceptibility of the site to water and wind erosion. Organic materials may have many effects on soil properties, including:

- degree of structure;
- water holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction of soil erosion potential;
- soil temperature.

Organic matter may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and the degree of mineralization of the material.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are needed to prepare the site and apply the acidifying agent and reducing agent.

Information Requirements

- characterization and concentration of metals, particularly selenium (Treatment of selenium is incompatible with treatment of all other metals; oxidation state of metallic ions);
- depth, profile, and areal distribution of contamination;
- soil pH;
- soil organic matter;
- clay content of soil;
- acidification and reduction reaction rates;
- trafficability of soil and site.

Sources of Information

Griffin, R.A., and Shimp, N.A., 1978; Sharma, S., and Singh, R., 1983.

3.4.1.2.4 Sodium Reduction/Dehalogenation for PCBs and Dioxins

Description

Several processes to detoxify PCB's and, potentially dioxins have been developed in the past several years. All employ a sodium-based chemical reagent to remove chlorine from the very stable PCB and dioxin molecules. The residue structures are generally non-toxic or of lower toxicity than the original compound. These processes were originally developed for the treatment of PCB-containing oils; several have been suggested for application to contaminated soils. The sodium strips off the chlorine to form sodium chloride (common salt).

One process, Acurex, follows a two-step procedure. First, dioxins (or PCB's) are extracted from the soil with a special blend of solvents. The solvents are then treated with a proprietary sodium-based reagent to destroy the contaminants (Mille, G.J., 1982). A second process, developed by the Franklin Research Institute, applies a reagent directly to the soil. The reagent is a chemically-modified sodium polyethylene glycol (NaPEG) complex. The reagent is quite stable, does not contain metallic sodium, and is not sensitive to small quantities of water (Franklin Research Institute, 1981).

Wastes Amenable to Treatment

PCB's and dioxins are detoxified. Other halogenated compounds will also be attached by the reagents.

Status of Technology

The technology has been applied to the treatment of PCB-containing oils, but is still in the developmental stage with respect to soil decontamination.

Ease of Application

The reagents are liquids and should be applied relatively easily. They will react with excess moisture and thus must be applied under carefully controlled conditions.

Potential Achievable Level of Treatment

Results with PCB oils have shown high levels of detoxification. The same levels are potentially realizable in soils.

Reliability

Once the compounds are dechlorinated, there is no mechanism to reverse the reaction. If the application is successful in the first place, no further retreatment should be needed.

Secondary Impacts

The reagents are powerful reducing agents and may react with soil organic matter. The consequences of such reactions are unknown at present.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are needed. Some sort of temporary cover might be needed to keep rain off of the treatment area until the reactions are complete. Soil may have to be drained or tilled and allowed to dry. Reducing agents are needed in sufficient quantity to react with the target contaminants and with other waste and natural constituents.

Information Requirements

- depth, profile, and areal distribution of contamination;
- soil moisture content.
- soil temperature

Source of Information

Mille, G.J., 1982; Franklin Research Institute, 1981.

3.4.1.3 Polymerization

Description

A polymer is a large molecule built up by the repetition of small, simple chemical units. A polymerization reaction is the conversion of a particular compound to a larger chemical multiple of itself (Kirk Othmer Encyclopedia of Chemical Technology, 1982). The resulting polymer often has different physical and chemical properties from the initial unit and could be less mobile in the soil system.

It has been demonstrated that naturally occurring iron and sulfates in contaminated soil may catalyze initial polymerization of contaminants. Treatment solutions containing sulfate-related constituents have been successfully used in polymerization reactions in the soil (Williams, 1982). Acrylate monomer (4200 gallons) contaminating glacial sand and gravel layers was polymerized in-place by injecting a catalyst, activator, and wetting agent.

Mercer, B.W., et al. (1970), working with grouting materials and polymeric agents, found the process of in-place immobilization with these agents expensive and complicated by the logistics of obtaining widespread coverage without an excessive number of injection wells.

Wastes Amenable to Treatment

Chemical polymerization is most effective for immobilization of organic constituents, preferably those with more than one double bond. General categories of constituents, applicable to polymerization include aliphatic, aromatic, and oxygenated monomers, such as styrene, vinyl chloride, isoprene, acrylonitrile, etc. For multi-organic contamination, catalysts and activators necessary to achieve polymerization may interact with one another.

Status of Technology

Experimental studies have been conducted in the field.

Ease of Application

A 2:1 ratio of volume of catalyst and activator to volume of contaminant is used. The catalyst and activator should be applied in two applications and applied separately to prevent reactions before contact with wastes. A wetting agent is added to promote rapid and uniform dispersion of solutions through the contaminated area. If ground temperature falls below 50°F, it may be necessary to warm the treatment solution to 50°F before use. Because of the acidic nature of treatment reagents, corrosion-resistant application equipment is required.

If the surficial zone is too shallow to tolerate sufficient injection pressure for dispersing catalyst and activator solutions, installation of exfiltration galleries (e.g., a 2-inch diameter perforated PVC casing, buried in trenches below ground surface across the contaminated zone) is required. A riser pipe and manifold header connect each gallery to solution tanks which contain catalyst and activator.

This technology is moderate to difficult to apply. In a field study, it was found that obtaining widespread coverage was difficult without an excessive number of injection wells.

Potential Achievable Level of Treatment

The level of treatment achievable is variable, depending on the waste and soil conditions. The potential for long-term immobilization is unknown at this time.

Reliability of Method

The reliability of the treatment is unknown since there is no information on its long-term effectiveness.

Secondary Impacts

The polymerized area may exhibit decreased infiltration and permeability.

Equipment and Exogenous Reagents

Catalysts and activators are needed. Vendors should be consulted as to the equipment to be used.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- potential for polymerization of waste constituents;
- polymerization products;
- depth, profile, and areal distribution of constituents;
- iron and sulfate content in soil;
- catalysts and activators present in soil;
- trafficability of soil and site.

Sources of Information

Kirk Othmer Encyclopedia of Chemical Technology, 1982; Mercer, B.W., et al., 1970; Williams, E.B., 1982.

3.4.2 Biological

Biodegradation is an important environmental process causing the breakdown of organic compounds. It is a significant loss mechanism in soil in the mineralization process by which organics are converted to inorganics.

Micro-organisms, principally bacteria, actinomycetes, and fungi, are the most significant group of organisms involved in biodegradation, and soil environments contain a diverse microbial population. The parameters influencing the rate of biodegradation are of two types:

1) those that determine the availability and concentration of the compound to be degraded or that affect the microbial population site and activity; and

2) those that control the reaction rate.

Important parameters affecting biodegradation include pH, temperature, soil moisture content, soil oxygen content, and nutrient concentration, among many others (Bonazountas and Wagner, 1981).

Table 3-19 shows rate constants of organic compounds in soil. Table 3-20 shows rates in anaerobic systems.

Biological treatment methods are directed toward enhancing biochemical mechanisms for detoxifying or decomposing hazardous waste materials in contaminated soils. Soil micro-organisms, principally the bacteria, actinomycetes, and fungi, are important in decomposition or detoxification processes. Therefore, treatments applied to the soil to enhance biological processes must not alter the physical environment in such a way that it would severely restrict microbial growth and/or biochemical activity. In general, this means that soil temperatures should be between 50°C and 60°C (Atlas and Bartha, 1981); soil water potential should be greater than − 15 bars (Sommers et al., 1981), pH should be between 5 and 9 (Alexander, 1977; Atlas and Bartha, 1981), and oxidation-reduction (redox) potential should be between pe + pH of 17.5 to 2.7 (Baas and Becking et al., 1960). Soil pH and redox boundaries should be carefully monitored when chemical and biological treatments are combined. With these restrictions in mind several treatments are considered, both tried and theoretical, which may enhance microbial activity in hazardous waste contaminated soil.

TABLE 3-19. BIODEGRADATION RATE CONSTANTS FOR ORGANIC COMPOUNDS IN SOIL (day^{-1})

Compound	Test Method	
	Die-Away	$^{14}CO_2$ Evolution
Aldrin, Dieldrin	0.013	
Atrazine	0.019	0.0001
Bromacil	0.0077	0.0024
Carbaryl	0.037	0.0063
Carbofuran	0.047	0.0013
Dalapon	0.047	
DDT	0.00013	
Diazinon	0.023	0.022
Dicamba	0.022	0.0022
Fonofos	0.012	
Glyphosate	0.1	0.0086
Heptachlor	0.011	
Lindane	0.0026	
Linuron	0.0096	
Malathion	1.4	
Methyl parathion	0.16	
Paraquat	0.0016	
Parathion	0.029	
Phorate	0.0084	
Picloram	0.0073	0.0008
Simazine	0.014	
TCA	0.059	
Terbacil	0.015	0.0045
Trifluralin	0.008	0.0013
2,4-D	0.066	0.051
2,4,5-T	0.035	0.029

Source: Lyman, W.J., et al., 1982.

TABLE 3-20. BIODEGRADATION RATE CONSTANTS FOR ORGANIC COMPOUNDS IN ANAEROBIC SYSTEMS (day^{-1})

Compound	In Soil		In Sewage Sludge
	Die-Away	$^{14}CO_2$ Evolution	
Carbofuran	0.026		
DDT	0.0035		
Endrin	0.03		
Lindane		0.0046	
PCP		0.07	
Trifluralin	0.025		
Mirex			0.0192
Methoxyclor			9.6
2,3,5,6-Tetrachlorobenzene			12.72
Bifenox			6.27

Source: Lyman, W.J., et al., 1982.

3.4.2.1 Modification of Soil Properties

Since the activity of micro-organisms is so dependent on soil conditions, modification of soil properties is a viable method to enhance the microbial activity in the soil. These soil properties are: soil moisture, soil oxygen content, soil pH, and nutrient content. Details of how to apply the soil modification techniques are given in Section 4.

3.4.2.1.1 Soil Moisture

Description

When natural precipitation is insufficient to maintain soil moisture within a range that is near optimal for microbial activity, irrigation may be necessary. Although many microbial functions continue in soils at −15 bars or drier, optimum biochemical activity is usually observed at soil water potentials of −0.1 to 1.0 bar (Sommers et al., 1981).

In a review of soil water potential on decomposition processes in soils, including pesticide degradation, Sommers et al. (1981) suggested that the effect of soil water potential on pesticide degradation is to alter general microbial activity and to affect the kinds of micro-organisms which are metabolically active in the soil. Ou et al. (1983) observed rapid mineralization of methyl parathion in soils at −0.1 and −0.33 bar soil moisture tension, along with the formation of bound residues. The ratio of the degradation products (p-nitro-phenol to p-aminophenol) increased as the soils became drier. In dry soil (−15 bar), mineralization of methyl parathion and bound residue formation were slower. Limited experimentation with the effects of soil moisture on degradation indicates that degradation rates are highest at soil water potential between 0 and −1 bar.

The degradation of hazardous organic compounds may be accelerated by soil moisture optimization, and this approach may be sufficient to bring about required degradation, especially for constituents relatively easy to degrade. However, more rapid treatment of the contaminated soil may be achieved when moisture augmentation is used in combination with other techniques.

Wastes Amenable to Treatment

Biodegradable organic compounds are amenable to this treatment.

Status of Technology

Moisture control is widely practiced in agriculture. However, little information is available on the use of moisture control to stimulate biological degradation of hazardous materials in soil. Most experimental work in the laboratory on pesticides and other xenobiotic compound degradation has been conducted at or near optimal soil moisture.

Ease of Application

An irrigation and drainage system is required. Irrigation water is applied using standard irrigation practices. Irrigation should be applied frequently in relatively small amounts, without exceeding field capacity, to minimize leaching. Depending on the ease of controlling water at the site and on the availability of a suitable water source (e.g., transport distance, drilling of new wells, availability and cost of energy for pumping), it may be easy or difficult to apply this technology. Controls for erosion and proper drainage due to runoff are necessary.

Potential Achievable Level of Treatment

The achievable level of treatment may be low to high, depending on the biodegradability of waste constituents and suitability of the site and soil for effective moisture control. The effectiveness of this technology may be enhanced by the use of other treatment techniques to increase biological activity.

Reliability of Method

This technology is reliable in that it has been used in agriculture, but retreatment is necessary.

Secondary Impacts

Leaching of soluble hazardous compounds may occur. Erosion may also be a problem.

Equipment and Exogenous Reagents

An irrigation system and water are required.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil moisture;
- other soil properties for biological activity (pH, oxygen content, nutrient content, organic matter, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Bonazountas, M., and Wagner, J., 1981; Atlas and Bartha, 1981; Sommers, L.E., et al., 1981; Alexander, M., 1977; Bass et al., 1960; Lyman, W.J., et al., 1982; Ou et al., 1983.

3.4.2.1.2 Soil Oxygen Content for Aerobic Biodegradation

Description

One reason for the common practices of tilling and/or draining the soil in agriculture is to stimulate organic matter decomposition in an aerobic environment so that nutrients will be mineralized and made available for plant assimilation. Aerobic metabolism is more energy-efficient, and microbial decomposition processes are, in general, more rapid under aerobic conditions. Although the decomposition of some xenobiotic organic compounds appears to require anaerobic metabolism, the majority of organisms in soils shown to be active in pesticide and other xenobiotic compound decomposition are aerobic (Alexander 1977; Pal et al., 1980, Baker and Mayfield, 1980; Brunner and Focht, 1983; Sims and Overcash, 1981). In many instances, therefore, assuring the aerobiosis of the soil will enhance the rate of biological decomposition.

Tilling the soil for aeration is common practice in agriculture and has been recommended for hazardous waste-contaminated soil reclamation by practitioners and researchers (Arthur D. Little, Inc., 1976; Thibault and Elliott, 1979). Soils with high water tables that restrict aeration may also be drained using common agricultural techniques.

Wastes Amenable to Treatment

Organic wastes that are acted upon by micro-organisms under aerobic conditions are amenable to treatment. Most organics fall into this category of compounds.

Methods of Technology

In the field, tilling the soil for aeration is common practice in agriculture to enhance crop-residue degradation, and it has been recommended for hazardous waste-contaminated soil reclamation.

Ease of Application

If the site is too wet, a drainage system should be installed. The soil is tilled at periodic intervals to achieve aeration. Controls to prevent runon and runoff of precipitation are necessary. This technology is easy to difficult, depending on the characteristics of the soil and the site and the trafficability of the site.

Potential Achievable Level of Treatment

The level of treatment achievable is from low to high, depending on the biodegradability of the waste constituents and the suitability of the site and soil for maintenance of aerobic conditions.

Reliability of Method

Retreatment at periodic intervals is necessary to assure that the soil oxygen is at a sufficiently high level.

Secondary Impacts

Tillage will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements and tillers are necessary.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil oxygen content;
- other soil properties for biological activity (soil moisture, pH, nutrient content, organic matter, temperature, etc.);
- soil texture;
- trafficability of soil and site.

Sources of Information

Pal, et al., 1980; Baker, M.D., and Mayfield, 1980; Brunner, W., and Focht, D.D., 1980; Sims, R.C., and Overcash, M.R., 1981; Arthur D. Little, Inc., 1976; Thibault, G.T., and Elliott, N.W., 1979; Lyman, W., et al., 1982, Atlas and Bartha, 1981; Bass, J., et al., 1960.

3.4.2.1.3 Soil Oxygen Content for Anaerobic Biodegration

Description

There is increasing evidence that some halogenated xenobiotic compounds may be dehalogenated or completely degraded under anaerobic conditions (Sulflita, J.M., et al., 1982; Sulflita, J.M., and Tiedje, J.M., 1983; Horowitz, A., et al., 1983; Sulflita, J.M., et al., 1983; Kobayashi and Rittman, 1982; Pfaender and Alexander, 1972). Therefore, manipulation of contaminated soil to create an anaerobic, reducing environment to enhance the decomposition of certain hazardous waste constituents should be considered. Apparently, the redox potential (Eh) of the environment must be below 0.35V for significant reductive dechlorination to take place, but exact requirements depend upon the individual compounds being reduced (Kobayashi and Rittman, 1982). Reductive reactions may be catalyzed by both abiotic and biochemical means in anaerobic environments.

Once a recalcitrant compound has been altered by reductive reactions under anaerobic conditions, it may be more amenable to decomposition under aerobic conditions. For example, the reductive dechlorination of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) under anaerobic conditions to 2,4-dichlorophenoxyacetic acid (2,4-D) which is readily degraded in the soil under aerobic conditions has been described (Munnecke et al., 1982). Laboratory experimentation may show that anaerobic soil conditions followed by aeration may enhance biological decomposition of some hazardous waste constituents. However, Marinucci and Bartha (1979) evaluated weekly alterations between anaerobic and aerobic conditions for enhancement of biodegradation of trichlorobenzenes in soil and found no improvement in mineralization rates. The trichlorobenzenes were mineralized most rapidly under continuous aerobic conditions. Other classes of compounds may not follow this pattern, and more research is needed to further evaluate the potential for treatment by using alternating anaerobic and aerobic conditions. Longer periods between alternation may be appropriate.

Arthur D. Little, Inc. (1976), also reported that the only proven method of creating anaerobic conditions is to dike and flood the soil in a fashion similar to that used to grow rice. They cite unpublished work by W. Farmer at the University of California at Riverside in which a 1.5-acre DDT-contaminated field was amended with organic matter, flooded, and the soil temperature increased. Complete transformation of the DDT to DDD was observed in 18 days. They suggest that, without this treatment, the transformation to DDD would have taken more than 2 years. Flooding the soil presents opportunities for leaching of hazardous materials from contaminated soil and is probably not advisable in most hazardous waste-contaminated soils. However, it should be possible to lower the redox potential of the soil by adding excessive amounts of readily biodegradable organic matter, compacting the soil to reduce oxygen diffusion through large soil pore spaces, keeping the soil wet without exceeding the gravitational water potential (field capacity), and perhaps deep mulching to impair oxygen diffusion to the soil surface.

Applications of this method of inducing anaerobiosis have not been identified in the literature as used either in the field or under laboratory conditions. Reductive dehalogenations or other reductive reactions that lead to decomposition or detoxification of specific hazardous waste constituents should be verified from the literature or from experimentation before this treatment is used.

Wastes Amenable to Treatment

Organic wastes that are biodegradable under anaerobic conditions, e.g., halogenated compounds, are amenable to this treatment.

Status of Technology

In the field, this technology is only conceptual. Neither are there any reported laboratory studies using this technique.

Ease of Application

Organic materials are applied and incorporated into the soil. Irrigation water is applied using standard irrigation practices. Irrigation water should be applied in amounts large enough to create anaerobic sites in the soil, but not to cause leaching. Mulches may also be applied to act as a barrier to oxygen diffusion into the soil. The soil may be compacted to reduce porosity. Runon and runoff controls are necessary. This technology involves a complex combination of soil manipulations (i.e., moisture control, organic amendment, compaction, and mulching) and may range from moderate to difficult to apply.

Potential Achievable Level of Treatment

Depending on the degradative pathway of the constituents, the achievable level of treatment may range from low to high. This technology may result only in partial degradation, requiring the establishment of aerobic conditions to complete treatment.

Reliability of Method

Retreatment is necessary as frequently as required to maintain anaerobic conditions.

Secondary Impacts

This technology may result in the formation of toxic volatile forms of metals (e.g., methylated mercury and arsines), hydrogen sulfide, and other nuisance odor compounds. Leaching of hazardous constituents may also occur if water addition is not carefully controlled. Organic materials may have many effects on soil properties, including:

- degree of structure;
- water-holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction in soil erosion potential;
- soil temperature.

Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material.

Equipment and Exogenous Reagents

Power implements, compactors and an irrigation system are necessary. The exogenous materials required are irrigation water and organic materials, e.g., mulches.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil oxygen content;
- other soil properties for biological activity (soil moisture, pH, nutrient content, organic matter, temperature, etc.);
- soil water holding capacity;
- suitability of site to flooding and drainage;
- trafficability of soil and site.

Sources of Information

Sulflita, J.B., et al., 1982; Sulflita, J.M., et al., 1983; Sulflita, J.M., and Tiedje, J.M., 1983; Horowitz, A., et al., 1983; Sulflita, J.M., et al., 1983; Kobayashi, H., and Rittman, B.E., 1982; Pfaender, F.K., and Alexander, M., 1972; Munnecke, D.M., et al., 1982; Marinucci, A.C., and Bartha, R., 1979; Arthur D. Little, Inc., 1976; Alexander, 1977; Atlas and Bartha, 1981; Bass et al., 1960; Lyman et al., 1982; Bonazountas, M., and Wagner, J., 1981; Munnecke, D.M., 1980.

3.4.2.1.4 Soil pH

Description

Depending on the nature of the hazardous waste components contaminating the soil, it may be advantageous to optimize the soil pH for a particular segment of the microbial population, since microbial community structure and activity are affected by soil pH (Gray, 1978; Alexander, 1977). Some fungi have a competitive advantage at slightly acidic pH, while actinomycetes flourish at slightly alkaline pH (Alexander, 1977). Soil pH has also been shown to be an important factor in determining the effect various pesticides have on soil micro-organisms (Anderson, 1978). Near neutral pH values are probably most conducive to microbial functioning in general. The recent discovery that fungal metabolism of polynuclear aromatics (PNAs) is qualitatively similar to mammalian metabolism in that mutagenic arene oxides (epoxides) are produced as initial oxidation products (Cerniglia and Gibson, 1979; Cerniglia et al., 1979) suggests that fungal degradation of PNAs in the environment should be discouraged. Although the effect of soil pH on the formation of epoxides from PNAs has not been demonstrated, it may be advantageous to maintain pH near neutrality to encourage a relatively higher bacterial activity in soils contaminated with these compounds.

It may be necessary to treat contaminated soil with crushed limestone or lime products to raise the pH to the desired range, or with acid-producing materials or sulfur to lower the pH. Methods for determining the lime requirement of agricultural soils that take into account the buffering capacity of the soil (McLean et al., 1966; McLean, 1982) have been developed, but guidelines for reducing soil pH are not readily available, and the addition of acidifying agents must be determined experimentally in the laboratory.

Wastes Amenable to Treatment

Organic wastes that are biodegradable are amenable to this treatment.

Status of Technology

Liming is a common agricultural practice. Acidification is much less commonly required.

Ease of Application

A lime requirement test may be performed to determine loading rate for increasing soil pH. Acidification requirements for a particular soil have to be determined experimentally. Buffering capacity of the waste must also be considered.

Thorough mixing is required in the zone of contamination to effect pH change. Because the soil is tilled, runoff and minor controls are necessary to control drainages and erosion. This technology ranges from easy to difficult to apply, depending on the trafficability of the soil and the depth of contamination.

Potential Achievable Level of Treatment

The achievable level of treatment is high, depending on the biodegradability of the wastes and the suitability of the site and the soil.

Reliability of Method

Reliming or reacidification is necessary as treatment progresses.

Secondary Impacts

Dissolution or precipitation of materials within the soil are affected by changes in soil pH. Care must be taken to assure that hazardous materials do not increase in mobility due to the raising or lowering of soil pH. Tillage increases the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Applicators, tillers, and power implements are required. Depending on the wastes and the soil characteristics, liming or acidifying material is required.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil pH;
- other soil properties for biological activity (oxygen content, soil moisture, nutrient content, organic matter, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Gray, 1978; Alexander, 1977; Anderson, 1978; Cerniglia, and Gibson, 1979; Cerniglia, et al., 1979; McLean, 1982; McLean, et al., 1966.

3.4.2.1.5 Soil Nutrients

Description

Although most micro-organisms are capable of very efficient extraction of inorganic nutrients from their environment, their activity may be limited by nutrient availability. This is especially true if available carbon is in large excess relative to the nitrogen and/or phosphorus required by the micro-organisms that degrade it. Determination of soil organic carbon, organic nitrogen, and organic phosphorus allows the determination of its C:N:P ratio and an evaluation of nutrient availability. If the ratio of organic C:N:P is wider than about 300:15:1 and available (extractable) inorganic forms of N and P do not narrow the ratio to within these limits, supplemental nitrogen and/or phosphorus should be added (Alexander, 1977; Kowalenko, 1978). Excesses or deficits of nitrogen or phosphorus brought about by addition of any organic amendments should be taken into account, and commercial fertilizers can be used to make up any deficit.

Adding fertilizer to hasten the decomposition of crop residues is used in agriculture (Alexander, 1977), and this procedure has been used in the treatment of hazardous waste (oil spill)-contaminated soils (Thibault, and Elliott, 1980). Skujins, et al. (1983) studied the biodegradation of waste oils at a disposal site whose soils were amended with calcium hydroxide, phosphate, and urea. Within 4 years, 90 percent of the applied oil (added 7.5 percent by weight to the surface 10 cm) was degraded.

Wastes Amenable to Treatment

Biodegradable organics are amenable to this treatment.

Status of Technology

In the field, this technology is commonly used in agriculture. It has also been used in the treatment of oil wastes.

Ease of Application

Fertilizers are added to the soil using standard agricultural methods. Depending on the nutrient type, physical state, solubility of the fertilizer, and depth of contamination, the fertilizer is incorporated into the soil as necessary. Sufficient N and P is applied to ensure that these nutrients do not limit the microbial and metabolic activity. Controls to manage the runon and runoff from the site are necessary to prevent drainage and erosion problems. This technology ranges from easy to difficult to apply, depending on trafficability considerations.

Potential Achievable Level of Treatment

If nutrient availability is limiting or retarding microbial degradation or detoxification of organic hazardous waste constituents, the achievable level of treatment would be high if the site and soil characteristics are suitable.

Reliability of Method

Retreatment may be necessary at intervals as nutrients are used up in the process. Liming and reliming may be necessary to maintain optimal pH for biological activity.

Secondary Impacts

Caution must be used in the application of nitrogen to the soil to avoid excessive application. Nitrate or other forms of nitrogen in the soil oxidized to nitrate may be leached to groundwater. Also, some nitrogen fertilizers tend to lower the soil pH, necessitating a liming program to maintain pH optimal for biological activity. Tillage will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are required to apply the fertilizer to the soil.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil nutrient (concentration of all essential nutrients, particularly limiting nutrients);
- other soil properties (pH, soil moisture, oxygen content, organic matter, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Alexander, 1977; Kowalenko, 1978; Thibault and Elliott, 1980; Skujins, et al., 1983; Bass et al., 1960; Bonazountas and Wagner, 1981; Lyman, et al., 1982; Atlas and Bartha, 1981.

3.4.2.2 Addition of Non-specific Organic Amendments

Description

Stimulating general soil microbial activity and population size through organic matter addition improves the opportunities for selection of organisms that can degrade hazardous waste components. High microbial activity provides opportunity for cometabolic processes to act on recalcitrant hazardous waste components. Addition of manures, plant materials, and/or wastewater treatment digester sludge at levels characteristic of composting may prove valuable to biological treatment of hazardous waste-contaminated soils (Kaplan, and Kaplan, 1982a; Doyle and Isbister, 1982).

Extensive laboratory research has shown that supplemental carbon and energy sources can stimulate the metabolism of xenobiotic, often recalcitrant compounds. The breakdown or transformation of these compounds can be through cometabolism (Alexander, 1981), or metabolism of the compound may simply be stimulated by the supplemental carbon and energy source (Yagi and Sudo, 1980). Composting of contaminated soil has been shown to degrade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), while the ring structure of 2,4,6-trinitrotoluene (TNT) was not mineralized. The TNT residues were apparently strongly sorbed to the compost (Doyle and Isbister, 1982). Camoni, et al., (1982) demonstrated that addition of organic compost to soil had no significant effect on the half-life (1 year) of 2,3,7,8-TCCD in soil. The degradation of pentachlorophenol and pentachloronitrobenzene in a laboratory composting system has also been studied (Sikora, et al., 1982).

Laboratory experimentation may be needed to determine the biochemical fate of given hazardous compounds in organically enriched soil or compost, and the environmental hazards associated with any residues evaluated (Kaplan and Kaplan, 1982b). Residues may be more or less toxic than the parent compounds. Residues of hazardous compounds may not be extractable from organically enriched soil using ordinary solvents, suggesting strong binding to organic matter or other soil constituents (Doyle and Isbister, 1982; Khan, 1982; Wallnöfer, et al., 1981; Bartha, 1980; Stevenson, 1972). Enzymatic activities of soil micro-organisms can be responsible for coupling xenobiotic compounds and their breakdown products to soil humic materials (Bollag, 1983; Bollag, et al., 1983; Sjobland and Bollag, 1981; Liu, et al., 1981; Sulflita and Bollag, 1980; Bollag, et al. 1980; Bollag, et al. 1978). Careful monitoring for bound hazardous organic compounds, including toxic metabolites of hazardous parent compounds should be performed. Humus-bound xenobiotic compounds may be slow to mineralize or be transformed to innocuous forms (Khan, 1982; Chowdhury, et al., 1981). In such cases, increasing the humic content of the soil may not be the method of choice.

Microbial decomposition of humic matter that contains bound hazardous organic compounds can release these compounds to the soil solution, where they are subject to leaching, volatilization, or reattachment to soil organic matter. This potential mobility of bound hazardous compounds suggests that treatment is not complete until their absence or safe level in the soil can be demonstrated (Bartha, 1980; Saxena and Bartha, 1983b; Khan and Iverson, 1982).

No examples of field trials of this treatment technique are available. Doyle and Isbister (1982) observed 55 percent degradation of RDX in compost incubated in a greenhouse in 6 weeks. In the same study, TNT levels were reduced by more than 99 percent within 3 weeks, but very little decomposition (mineralization) was observed.

Aerobic heterotrophic bacteria oxidize arsenite (As^{+3}) to arsenate (As^{+5}) with the consumption of 0_2. An available reserve of organic matter must be present in the soil for the oxidation to occur. Therefore, when arsenite contaminates a soil in concentrations that are below toxic levels for soil heterotrophs, it will be possible to oxidize the arsenite to arsenate by amending the soil with readily available organic matter and maintaining aerobic conditions in the soil. Oxidation of arsenite in laboratory soil perfusion systems has been described by Quastel and Scholefield (1953). The microbial biochemistry of arsenic has been reviewed by Alexander (1977) and Konetzka (1977). Further treatment with ferrous sulfate will form highly insoluble $FeASO_4$.

Wastes Amenable to Treatment

Biodegradable organic wastes and arsenite wastes are amenable to this treatment.

Status of Technology

There are no examples of field trials. Chemical precipitation is usually used to treat arsenite wastes at landfill sites. Extensive laboratory research has shown that supplemental carbon and energy sources can stimulate metabolism of even recalcitrant compounds. Experimental soil systems have demonstrated the microbial oxidation of arsenite to arsenate.

Ease of Application

The quantity of organic material required must be determined in treatability studies. Nonspecific, readily biodegradable organic matter should be added and mixed into the soil as dry materials or as slurries. The soil moisture level should be optimized, and frequent mixing is required to maintain aerobic conditions. Runon and runoff controls are required. This technology is easy or difficult, depending on the trafficability of the soil and site, and the depth of contamination.

Potential Achievable Level of Treatment

The potential achievable level of treatment ranges from low to high, depending on the solubility, sorption, and biodegradability of the organic constituents in the waste. Some arsenite may be bound to the soil and will not be available for oxidation. Available (extractable) arsenite should be quickly and completely oxidized.

Reliability of Method

This technolgy may require reapplications to complete treatment.

Secondary Impacts

Hazardous constituents may be initially bound to organic materials, but later released as organic materials decompose.

Under anaerobic conditions, the added organic matter may result in the reduction and methylation of arsenic to volatile forms. Anaerobic conditions must be avoided. However, anaerobic microsites are known to exist even in well-aerated soil, and some volatile metal compounds may be produced even in carefully managed soils. Tillage will increase the susceptibility of the site to erosion.

Organic materials may have many effects on soil properties, including:

- degree of structure;
- water-holding capacity;
- bulk density;
- immobilization of nutrients, hindering degradation of organic wastes;
- reduction in soil erosion potential;
- soil temperature.

Organic materials may also result in excessive nitrate levels in receiving waters, depending on the nitrogen content and degree of mineralization of the material.

Equipment and Exogenous Reagents

Power implements, tillers, applicators, and proper drainage are required. The exogenous reagent required is organic material.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- soil organic matter;
- other soil properties (pH, soil moisture, oxygen content, nutrient content, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Kaplan and Kaplan, 1982a and 1982b; Doyle, Isbister, 1982; Alexander, 1981; Yagi, and Sudo, 1980; Camoni, et al., 1982; Sikora, et al., 1982; Khan, 1982; Wallnöfer, et al., 1981; Bartha, 1980; Stevenson, 1982; Bollag, 1983; Bollag, et al., 1983; Sjobland and Bollag, 1981; Liu, et al., 1981; Sulflita and Bollag, 1980; Saxena and Bartha, 1983a and 1983b; Khan and Iverson, 1982; Quastel and Scholefield, 1953; Konetzka, 1977; Lyman, et al., 1983; Bonazountas and Wagner, 1981; Sikora L.J., et al., 1982.

3.4.2.3 Analog Enrichment for Cometabolism

Description

Adding a chemical analog of a hazardous compound to a contaminated soil or to culture media can accomplish cometabolism of the hazardous compound (Sims and Overcash, 1981; Pal et al., 1980; Furukawa, 1982; Focht and Alexander, 1970). Apparently, enzymes proliferated by micro-organisms to metabolize an energy-yielding substrate with structural similarity to a recalcitrant xenobiotic compound can, in certain cases, transform the recalcitrant molecule cometabolically (Alexander, 1981). For compounds where the transformation product of the cometabolic process is not hazardous or is degradable by other organisms in the soil microbial community, analog enrichment may be an effective treatment for contaminated soil.

Sims and Overcash (1981) used analog enrichment with phenanthrene to increase the rate of degradation of benz(a)pyrene, resulting in a decrease of 35 percent in the half-life. Biphenyl has been used to stimulate cometabolic degradation of PCBs (Furukawa, 1982).

Close chemical analogs to hazardous compounds or their degradation products may be hazardous. Therefore, care must be used in selecting and using analog exogenous agents for treatment.

Wastes Amenable to Treatment

Organic waste containing constituent(s) having analogs with high rates of degradation by organisms without producing toxic products are amenable to treatment.

Status of Technology

No information is available on the field level. In the laboratory, studies that are limited in number and range of compounds have shown that analog enrichment can accomplish cometabolism.

Ease of Application

Analog compounds are added in amounts large enough to stimulate microbial activity, but not enough to be toxic to microbial functions or to adversely affect public health and the environment. Treatability studies are required to determine the feasibility, loading rate, and effectiveness of the analog(s). The analogs may be applied as solids, liquids, or slurries and mixed thoroughly with the contaminated soil. Fertilization may be required to maintain microbial activity. Controls may be necessary to prevent drainage and erosion problems. This technology may range from easy to difficult to apply, depending on the trafficability and the depth of contamination.

Potential Achievable Level of Treatment

The level of treatment may range from low to high, depending on the susceptibility of the hazardous constituent to cometabolism.

Reliability of Method

The reliability of this technology is unknown.

Secondary Impacts

Tillage will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are required to apply the analog compounds.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-oganisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- availability of structural analog(s) to waste constituent(s);
- degradation pathway for analog;
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- other soil properties (pH, soil moisture, soil nutrient content, oxygen content, organic matter, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Sims and Overcash, 1981; Pal, et al., Furukawa, 1982; Focht, and Alexander, 1970; Alexander, 1981; Bonazountas and Wagner, 1981; Lyman, et al., 1982; Alexander, 1977.

3.4.2.4 Augmentation with Exogenous Acclimated or Mutant Micro-organisms

Description

Biological treatment methods described thus far have relied on the stimulation of microbial activity in the soil or on the natural selection of populations of micro-organisms, which can degrade toxic waste constituents. These approaches show considerable promise for treating many kinds of organic hazardous waste constituents. However, the metabolic range of the natural soil microbiota may not include the capability to degrade certain compounds or classes of compounds. In addition, microbial metabolic specialists may not develop large enough populations under limited substrate conditions to degrade xenobiotic compounds rapidly enough to meet treatment criteria. In situations such as these, it may be advisable to add exogenously grown micro-organisms to the soil. Microbial inoculants are available commercially with the broad range of metabolic capabilities, and experience in their use in both soil and aquatic systems contaminated with waste chemicals is expanding (Anonymous, 1981, 1982; Thibault and Elliot, 1980; Walton and Dobbs, 1980; Thibault and Elliot, 1979). Table 3-21 lists suppliers of biological products that have been or may be used to treat hazardous waste-contaminated soils. Frequently, the application of microbial amendments to the soil is combined with other treatment techniques such as soil moisture management, aeration, and fertilizer addition.

Laboratory trials have recently demonstrated the potential of exogenously grown, xenobiotic compound degrading bacteria to quickly degrade target compounds. Edgehill and Finn (1983) inoculated pentacholorophenol (PCP) degrading *Arthrobacter* and observed rapid degradation of PCP ($t_{1/2} < 1$ day) when the soil was incubated at 30°C. In soil treated under a roof where temperatures ranged from 8 to 16°C, PCP degradation was much slower, but mixed inoculated soil lost PCP faster than the control.

Kilbane et al. (1983) used repeated applications of a "genetically engineered" *Pseudomanas cepacia* with the ability to mineralize 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) obtaining 90 percent to essentially complete removal

TABLE 3-21. COMMERCIAL MICROBIAL AUGMENTATION PRODUCTS OR PROCESSES USED TO TREAT HAZARDOUS WASTE CONTAMINATED SOILS

Vendor	Address	Product Name(s)	Product Description	Treatment	Price	
					$/Unit	$/Acre
Flow Laboratories Environmental Cultures Division	Ingelwood, CA	DBC Plus; Types A, A-2,B,F, and H-1.	Formulated from specifically cultured bacteria preserved by freeze drying and air drying techniques.	25 lb/acre	10.50-15.80/lb	$263-395.00
General Environmental Science	Beachwood, OH	LLMO	Mixture of 7 bacterial strains (*Bacillus, Pseudomonas, Nitrosomonas, Nitrobacter, Cellulomonas, Acrobacter, Rhodopseudomonas)* in liquid suspension.	(Site dependent)	$16.00/gallon	
Groundwater Decontamination Systems, Inc.	Waldwick, NJ	GDS process	Technique involves circulating water from the soil into an environmentally controlled tank. Nutrients are added and the water is aerated. Treated water is returned to the soil. Air may be injected into the soil to stimulate further biodegradation.	(Site dependent)	$0.02/gal treated	
Polybac/Cytox Corporation	Allentown, PA; San Francisco, CA; Gonzales, FL	Polysoil process	Mutant bacteria formulation, nitrogen and phosphorus fertilizer, and biodegradable emulsifier.	100 lb. organisms + 400 lb. fertilizer and emulsifier if needed.		$3227-8067.00 per application[a]
		Chemical-biological augmentation process	Uses chemical treatment ahead of biological treatment to shorten treatment time (currently in experimental and demonstration stages).			$40,300-161,300 for total treatment
Sybron Biochemical	Birmingham, NJ; Salem, VA	Detoxsol	Formulation of mutant bacteria, buffer nutrients, growth stimulator, and detoxifying agents.	363 lb/acre	$27/lb	$9,801[b]

a. Includes labor, equipment, and products. Usually 2 to 6 applications required, depending on degradability with the Polysoil process.

b. Prices for treatment of areas larger than 2000 ft^2 are negotiable.

Source: Utah Water Research Laboratory of 2,4,5-T from contaminated soil within 6 weeks. When the 2,4,5-T was exhausted, the population of *P. cepacia* became undetectable, but when 2,4,5-T was added to the soil 12 weeks after initial treatment, regrowth occurred.

This method may be most effective against one compound or closely related compounds. Toxicity or the inability of the micro-organisms to metabolize a wide range of substrates may limit their effectiveness.

Recent research advancements in genetic engineering, particularly in interstrain and interspecies genetic transfer, hold out hope for development of organisms with extraordinary abilities to degrade xenobiotic compounds (Chakrabarty, 1982; Johnston and Robinson, 1982; Chakrabarty, 1980). More information is required, however, on the ability of genetically engineered organisms to survive, grow, and function in the soil environment (Stotsky and Krasovsky, 1981, Liang et al., 1982).

Wastes Amenable to Treatment

Compounds or classes of compounds which may be degraded by mutant or selected bacterial cultures which are available commercially are shown in Table 3-22.

State of Technology

This technology has been demonstrated in the laboratory and has been used in several full-scale soil decontamination operations. Case histories of treatment of chemical spill sites (oil spill, orthochlorophenol spill, and acrylonitrile spill) reported by Thibault and Elliott (1979, 1980) and Walton and Dobbs (1980) were deemed successful. However, some hazardous waste clean-up practitioners are skeptical about the use of this technology, since the soil environment is so important in determining microbial activity and hence the success of applying exogenous organisms (Anonymous, 1982). More information is required on the ability of exogenous organisms to service, grow, and function in the soil environment.

Ease of Application

Methods for application are determined in consultation with the vendor of the micro-organisms. The micro-organisms may be applied in liquid suspension or with a solid carrier. Depending on the method of application, runon and runoff controls may be necessary. The ease of application depends on the trafficability and the depth of contamination.

Potential Achievable Level of Treatment

With waste constituents that are susceptible to degradation by the added micro-organisms and when the site and soil are conducive to microbial activity, the potential level of treatment is high.

Reliability of Method

Relatively long periods of time may be required to complete treatment. Excessive precipitation may "wash out" the inoculum, necessitating retreatment.

Secondary Treatment

Tillage, if used, will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

These vary according to the micro-organisms used, as recommended by the vendor. Micro-organisms are usually applied by the vendors.

TABLE 3-22. COMPOUNDS OR CLASSES OF COMPOUNDS THAT HAVE BEEN (OR COULD BE) DEGRADED BY COMMERCIALLY AVAILABLE MICROBIAL AUGMENTATION PRODUCTIONS

Alcohols

- *n*-Butyl alcohol
- Dimethylaminoethanol

Alkyl Halides

- Ethylene dichloride (1,2-Dichloroethane)
- Methylene chloride (Dichloromethane)
- Propylene dichloride (1,2-Dichloropropane)

Amines

- Dimethylaniline
- Trimethylamine

Aromatic Hydrocarbons

- Divinyl Benzene
- Polynuclear Aromatic Hydrocarbons (PNA's)
- Styrene (Vinyl Benzene)

Chlorinated Aromatics

- Polychlorinated biphenyls (PCB's)

Esters

- Methacrylates

Ketones

- Acetone

Nitriles

- Acrylonitrile

Phenols

- Phenol
- Metachlorophenol
- Orthochlorophenol
- Pentachlorophenol
- Resorcinol (1,3-Benzenediol)
- t- Butylcatechol

Crude and refined oils

Emulsifiers

Detergents

Source: Utah Water Research Laboratory

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- metabolic capability of exogenously grown micro-organisms;
- pathogenicity to susceptible populations;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- depth, profile, and areal distribution of constituents;
- other soil properties (pH, soil moisture, nutrients, oxygen content, organic matter, temperature, etc.);
- trafficability of soil and site;
- climate, particularly precipitation.

Sources of Information

Anon., 1982; Thibault and Elliott, 1979, 1980; Walton and Dobbs, 1980; Edgehill and Finn, 1983; Kilbane, et al., 1983; Chakrabarty, 1980, 1982; Johnson and Robinson, 1982; Stotsky and Krasovsky, 1981; Bonazountas and Wagner, 1981; Lyman, et al., 1982; Alexander, 1977.

3.4.2.5 Application of Cell-free Enzymes

Description

Enzymes, produced by micro-organisms, which can transform hazardous compounds to nonhazardous or more labile products, could possibly be harvested from cells grown in mass culture and applied to contaminated soils. Crude or purified enzyme extracts are commonly used in industry either in solution or immobilized on glass beads, resins, or fibers to catalyze a variety of reactions, including the breakdown or transformation of carbohydrates and proteins. Munnecke, et al. (1982) discussed the enzymology of selected pesticide degradation, and suggested that extracted (cell-free) enzymes might be used to quickly transform pesticides in soils. They pointed out that a bacterial enzyme preparation has been used to detoxify organophosphate pesticide waste from containers (Munnecke, 1980), and that the enzyme parathion hydrolase hydrolyzed 1 percent parathion or diazinon within 24 hours in contaminated soil.

Enzyme activity can often be preserved in environments which are not hospitable to micro-organisms. Enzymes could possibly be used in soils with extremes of pH and temperature, high salinity, or high solvent concentrations, i.e., in soils where microbial growth may be restricted. In milder soil environments, enzymatic hydrolysis or oxidation of a compound may make it more susceptible to decomposition by the soil micribiota (Munnecke, et al., 1982).

To function outside the cell in the soil environment an enzyme must not require co-factors or co-enzymes — a requirement that will limit the application of many enzymes. Enzymes may also be chemically and/or biologically degraded. They may be leached out of the treatment zone, and they may be inactive or have lower activity if they are bound to clay or humus in the soil. Outside of biochemical and environmental constraints, logistics and costs for producing enzymes in large enough quantities may limit current use of this concept.

Wastes Amenable to Treatment

Organic wastes primarily are amenable to this treatment.

Status of Technology

Theoretically, enzymes would quickly transform hazardous compounds if they remained active in soil. There have been laboratory experiments with parathion hydrolase.

Little information is available on the use of this technique in soil. The only example at the present time is the work by Munnecke, et al. (1982). There is no information available from the field.

Ease of Application

For treatment of pesticides, application rates of 1 mg crude protein per 100 mg of pesticide in soil have been suggested (Munnecke, personal communication, July 1983). Thorough mixing with the soil is necessary. Enzymes are sprayed on soil in solution or suspension, or spread with solid carrier, using sprayers or fertilizer spreaders. The poor availability of appropriate enzymes for hazardous waste constituents makes application difficult. Depending on application method, controls to prevent runon and runoff may be necessary.

Potential Achievable Level of Treatment

Given the appropriate enzyme and if the enzyme remains active in the soil, the potential achievable level of treatment is high.

Reliability of Treatment

The reliability of this technology is unknown.

Secondary Impacts

Enzymatic degradation products may not be less hazardous than parent compound(s). Products may be more water soluble and/or mobile in the soil. Tillage, if used, will increase the susceptibility of the site to erosion.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are necessary for application of this treatment. Enzymes for treating hazardous waste constituents are not currently in bulk production. Although increases in the use of industrial enzymes have been projected (O'Sullivan, 1981), only eight companies accounted for 90 percent of worldwide production in 1981. Five of these companies are located in western Europe. Only 16 enzymes (primarily amylases, proteases, oxidases, and isomerases) accounted for 99 percent of the 1981 market. This information suggests that specialized enzyme production, even on a large scale, may be quite expensive. Current prices for bulk enzyme materials range in price from $1.45 to $164 per pound. If the enzyme can be produced through chemical synthesis, it will be much less expensive than if it is produced by micro-organsims in fermenters (Miles Laboratories, personal communication, July 1983).

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- micro-organisms present at site;
- biodegradability of waste constituents (half-life, rate constant);
- biodegradation products (particularly hazardous products);
- cell-free enzymetic activity for transformation of the compound(s) of interest;
- co-factor requirements of enzyme;
- stability of enzyme under soil environmental conditions;
- depth, profile, and areal distribution of constituents;
- other soil properties (pH, salinity, soil moisture, nutrients oxygen content, organic matter, temperature, etc.);
- trafficability of soil and site.

Sources of Information

Munnecke, et al., 1980, 1982; O'Sullivan, 1981.

3.4.3 Photolysis

Utilization of the lower atmosphere as a treatment medium requires an analysis of both the photoreaction potential and the volatility of the compounds of interest. Volatilization and dilution alone are not considered as acceptable treatment methods. An adequate assessment of the potential for the use of photodegradation requires information regarding the compound's atmospheric reaction rate (log $K_{OH^{\circ}}$) and anticipated reaction products. While this information is available for a selected number of compounds (Cupitt 1980; Lemaire et al., 1980), much more data are required if photodegradation is to become a viable treatment option.

If a compound is determined to be poorly photoreactive, e.g., a $t_{1/2}$ in the atmosphere greater than 1 day, volatilization suppression may be required to maintain safe ambient air concentrations at the site. Volatilization suppression techniques are described in Section 3.6.

Photodegradation is the use of incident solar radiation to carry out photoreaction processes. Both direct photolysis (photoreactions due to direct light absorption by the substrate molecule) and sensitized photo-oxidation (photoreactions mitigated by an energy-transferring sensitizer molecule) are possible under environmental conditions. Sensitized photoreactions are characteristically ones of photo-oxidation resulting in substrate molecule oxidation rather than substrate isomerism, dehalogenation, or dissociation characteristic of direct photolysis reactions.

The rate of photoreaction is influenced by the nature of light reaching the reaction medium, the absorption spectrum of the reacting species of sensitizer, the concentration of reacting species, the energy yield produced upon light energy absorption, the nature of the media in which the reaction is taking place, and the interactions that occur between the contaminant and its surroundings. Overall, reactions are a complicated function of the characteristics listed above. Photolysis reaction rates and breakdown products are only crudely understood.

Although the occurrence of the soil photoreaction of adsorbed chemicals has been identified, the importance of this reaction as compared to aqueous or vapor photoreactivity has not been identified. Soil photodecomposition will be of concern if the compound or compounds remain relatively stationary within the contaminated soil, e.g., high values of K_D (soil:water partition coefficient) and high values for K_W (air:water partition coefficient). Soil characteristics including soil organic content (Spencer, et al., 1980), transition metal content (Nilles and Zabik, 1975), and soil pigment content (Hautala, 1978) have been indicated as affecting photochemical reactions within soil systems. Moisture content and its effect upon chemical partitioning within the air/water/soil matrix within a soil system will also potentially have a great impact upon soil photoreactions (Burkhard and Guth, 1979; Hautala, 1978).

Information regarding the photolysis of pesticides in air is generally available due to the relatively high volatility of pesticides and the concern for their transport via the air medium. The major photoreaction taking place with pesticides in the atmosphere is oxidation (Crosby, 1971; Plimmer, 1971) involving the OH radical or ozone, of which the OH radical is the species of greatest reactivity (LeMaire, et al., 1982). Based on a first-order rate of reaction for vapor phase reactions with OH radical, the half life of a specific chemical species can be estimated if its OH radical reaction rate constant is known using:

$$t_{1/2} = 0.693/K_{OH^\circ}[OH^\circ]) \tag{3-16}$$

where

$t_{1/2}$ = time to decrease component concentration by 50% (s)

k_{OH° = OH radical reaction rate constant (cm^3/molecule-s)

$[OH^\circ]$ = atmospheric OH radical concentration (4×10^5 molecules/cm^3 = 6645×10^{-19} moles/cm^3)

A number of OH radical reaction rate constants as presented by Klopffer, (1980) and Cupitt, (1980), are given in Table 3-23. Table 3-24 presents additional constants, as given by Cupitt (1980), along with an estimation of the likelihood of a photolysis reaction occurring within the ambient atmosphere. Cupitt (1980) indicated that of all atmospheric removal mechanisms including physical, chemical, and photochemical, the photochemical reactions are of most significance for most classes of hazardous compounds and should be investigated further as a viable treatment option.

The use of photochemical reactions for the enhancement of compound biodegradation is an important area of interest for hazard mitigation from hazardous waste sites. Photolysis reactions are oxidative in nature and would be expected to aid in microbial degradation through the oxidation of resistant complex structures (Crosby, 1971; Sims and Overcash, 1983). Photoreactions are limited to soil surfaces due to light extinction within the soil system, but coupled to soil mixing, they may prove to be highly effective as an in-place treatment technique for relatively immobile chemical species.

TABLE 3-23. RATE CONSTANTS FOR THE HYDROXIDE RADICAL REACTION IN AIR WITH VARIOUS ORGANIC SUBSTANCES, K_{OH}° IN UNITS OF (MOLE-SEC)$^{-1}$

Substance	$\log_{air} k_{OH}^{\circ}$
Acetaldehyde	9.98
Acrolein	10.42
Acrylonitrile	9.08
Allyl chloride	10.23
Benzene	8.95
Benzyl chloride	9.26
Bis(chloromethyl)ether	9.38
Carbon tetrachloride	$<$ 5.78
Chlorobenzene	8.38
Chloroform	7.78
Chloromethyl methyl ether	9.26
Chloroprene	10.44
o-,m-,p-cresol*	10.52
p-cresol	10.49
Dichlorobromobenzene*	8.26
Diethyl ether	9.73
Dimethyl nitrosamine	10.37
Dioxane	9.26
Epichlorophydrin	9.08
1,2-epoxybutane	9.16
Epoxypropane	8.89
Ethanol	9.28
Ethyl acetate	9.06
Ethyl propionate	9.03
Ethylene dibromide	8.18
Ethylene dichloride	8.12
Ethylene oxide	9.08
Formaldehyde	9.78
Hexachlorocyclopentadiene	10.55
Maelic anhydride	10.56
Methanol	8.78
Methyl acetate	8.04
Methyl chloroform	6.86
Methyl ethyl ketone	9.32
Methylene chloride	7.93
Methyl propionate	8.23
Nitrobenzene	7.56
Nitromethane	8.81
2-nitropropane	10.52
n-nitrosodiethylamine	10.19
Nitrosoethylurea	9.89
n-propylacetate	9.41
Perchloroethylene	8.01
Phenol	10.01
Phosgene	nonreactive
Polychlorinated biphenyls	$<$ 8.78
Propanol	9.51
Propylene oxide	8.89
Tetrahydrofuran	9.95
Toluene	9.52, 9.56
Trichloroethylene	9.12
Vinylidene chloride	9.38
o-,m-,p-xylene*	9.98

Source: Adopted from Lemaire, et al. (1980) and Cupitt, (1980).

TABLE 3-24. ATMOSPHERIC REACTION RATES AND RESIDENCE TIMES OF SELECTED ORGANIC CHEMICALS

Compound	$k_{OH} \times 10^{12}$ (cm^3 molecule^{-1} sec^{-1})	Direct Photolysis Probability	Physical Removal Probability	Residence Time (Days)	Anticipated Photoproducts
Acetaldehyde^c	16	Probable	Unlikely	0.03-0.7^c	H_2CO, CO_2
Acrolein	44^a	Probable	Unlikely	0.2	OCH-CHO, H_2CO, HCOOH, CO_2
Acrylonitrile	2	–	Unlikely	5.6	H_2CO, HC(O)CN, HCOOH, CN^0
Allyl chloride	28^a	Possible	Unlikely	0.3	HCOOH, H_2CO, $ClCH_2CHO$, chlorinated hydroxy carbonyls, $ClCH_2COOH$
Benzyl chloride	3^a	Possible	Unlikely	3.9	OCHO, Cl; ring cleavage products chloromethyl-phenols
Bio(Chloromethyl) Ether	4^a	Possible	Probable	0.02-2.9^d	$HCl+H_2CO$, ClHCO, chloromethylformate
Carbon Tetrachloride	<0.001	–	Unlikely	$>11{,}000$	Cl_2CO, Cl^0
Chlorobenzene	0.4^a	Possible	Unlikely	28	Chlorophenols, ring cleavage products
Chloroform	0.1	–	Unlikely	120	Cl_2CO, Cl^-
Chloromethyl methyl ether	3^a	Possible	Probable	0.004-3.9^d	chloromethyl and methyl formate, ClHCO
Chloroprene	46^a	Probable	Unlikely	0.2	H_2CO, $H_2C{=}CClCHO$, OHCCHO, ClCOCHO, $H_2CCHCClO$, chloro-hydroxy acids, aldehydes
o,m,p-cresol^e	55	–	Unlikely	0.2	hydroxynitrotoluenes, ring cleavage products
Dichlorobenzene^e	0.3^a	Possible	Unlikely	39	chlorinated phenols, ring cleavage products
Dimethyl Nitrosamine	39^a	Probable	–	$\leqslant 0.3$	aldehydes, NO
Dioxane	3^a	–	Unlikely	3.9	$OHCOCH_2CH_2OCHO$, OHCOCHO oxygenated formates
Dioxin	–	Probable	–	–	–
Epichlorohydrin	2^a	Possible	Unlikely	5.8	H_2CO, OHCOCHO, $ClCH_2O(O)OHCO$
Ethylene Dibromide	0.25	Possible	Unlikely	45	Bi, $BrCH_2CH_2CHO$, H_2CO, Br HCO
Ethylene Dichloride	0.22	Possible	Unlikely	53	ClHCHO, $H_2CClCOCl$, H_2CO, $H_2CClCHO$
Ethylene Oxide	2^a	–	Unlikely	5.8	OHCOCHO
Formaldehyde^c	10	Probable	Unlikely	0.1-1.2^c	CO, CO_2
Hexachlorocyclo-pentadiene	59^a	Probable	–	0.2	Cl_2CO, diacyclchlorides, ketones, Cl•
Maleic Anhydride	60^a	Possible	Possible	0.1	CO_2, CO; acids, aldehydes and esters which should photolyze

TABLE 3-24. (Continued)

Compound	$k_{OH} \times 10^{12}$ (cm^3 $molecule^{-1}$ sec^{-1})	Direct Photolysis Probability	Physical Removal Probability	Residence Time (Days)	Anticipated Photoproducts
Methyl Chloroform	0.012	Possible	Unlikely	970	H_2CO, Cl_2CO, Cl•
Methylene Chloride	0.14	Possible	Unlikely	83	Cl_2CO, CO, ClHCO, Cl•
Methyl Iodide	0.004[a]	Possible	Unlikely	2900	H_2CO, I^0, ICHO, CO
Nitrobenzene	0.06[a]	Possible	Unlikely	190	Nitrophenols, ring cleavage products
2-Nitropropane	55[a]	Possible	Unlikely	0.2	H_2CO, CH_3CHO
N-Nitrosodi-ethylamine	26[a]	Probable	–	$\leq$0.4	aldehydes, nitroamines
Nitrosoethylurea	13[a]	Possible	–	$\leq$0.9	aldehydes, nitroamines
Nitrosomethylurea	20[a]	Possible	–	$<$0.6	aldehydes, nitroamines
Nitrosomorpholine	28[a]	Possible	–	$\leq$0.4	aldehydes, ethers
Perchlorethylene	0.17	Possible	Unlikely	67	Cl_2CO, $Cl_2C(OH)COCl$, Cl^0
Phenol	17[a]	–	Possible	0.6	dihydroxybenzenes, nitrophenols, ring cleavage products
Phosgene[f]	~0	–	Possible	–	CO_2, Cl^0, HCl
Polychlorinated Biphenyls	$<$1[a]	Possible	Unlikely	$>$11	hydroxy PCB's, ring cleavage products
POM (Benzo(a)-pyrene)	–	Possible	Probable	8	B(a)P-1,6-quinone
Propylene Oxide	1.3	–	Unlikely	8.9	$CH_3C(O)OCHO$, $CH_3C(O)CHO$, H_2CO, $HC(O)OCHO$
Toluene	6	–	Unlikely	1.9	Benzaldehyde, cresols, ring cleavage products, nitro compounds
Trichloroethylene	2.2	Possible	Unlikely	5.2	Cl_2CO, ClHCO, CO, Cl•
Vinyllidene Chloride	4[a]	Possible	Unlikely	2.9	H_2CO, Cl_2CO, HCOOH
o-,m-,p-xylene	16	–	Unlikely	~0.7	substituted benzaldehydes, hydroxy xylenes, ring cleavage products nitro compounds

a. Rate constant by method of Hendry and Kenley (1979).

b. Material is not expected to exist in vapor phase at normal temperatures. Residence time calculation assumes the chemical is substantially absorbed on aerosol particles and that the aerosol particles have a residence time of approximately 7 days.

c. The shorter residence time includes a photolysis rate as given in Graedel (1978).

d. Decomposition in moist air is expected. The shorter residence time includes the cited decomposition rate.

e. Values given are averages for the various isomers.

f. Reaction with O('D) is possible; $k = 3.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}, and [O('D)] = 0.2 molecules cm^{-3} implies a tropospheric lifetime of 440 years. In addition, slow hydrolysis is expected.

Source: Cupitt, L.T., 1980.

Photolysis of soil contaminants may be enhanced in 2 ways:

(1) by addition of proton donors, and
(2) by enhancing volatilization leading to photodegradation

3.4.3.1 Addition of Proton Donors

Description

Enhanced photodegradation of soil contaminants may be accomplished through the addition of various proton donor materials to the contaminated soils.

Photolysis of tetrachlorodibenz-p-dioxin (TCDD) on soil surfaces was reported by Crosby, et al. (1971) in the presence of suitable hydrogen sources in the form of polar solvents, and Plimmer, et al. (1973) indicated that methanol used as a solvent for TCDD photo-oxidation also acted as a hydrogen donor in the photolysis reaction.

Investigations of feasible in-place treatment methods for contaminated areas surrounding the TCDD release which occurred near Seveso, Italy, in 1976 have been reported by a number of authors. Wipf, H.K., et al. (1978) investigated the use of alternative hydrogen donors for the photo-oxidation of TCDD. Solutions of 80 percent olive oil and 20 percent cyclohexane at 350 L/ha and 40 percent aqueous emulsion with 4 percent biodegradable emulsifying agent at 400 L/ha were found to produce a thin film on vegetation and other smooth surfaces to provide a maximum reaction surface for TCDD photolysis. TCDD reductions in excess of 60 percent were observed within 48 hours after treatment. Under laboratory conditions, the oil and emulsion solutions reduced the half life of TCDD by a factor of 25 upon irradiation with simulated sunlight.

Liberti, et al. (1978) reported a 1:1 solution of ethyl oleate and xylene used as hydrogen donors also resulted in complete degradation of TCDD on building surfaces in approximately 1 hour at 2 mW/cm^2 and 72 hours at 20 $\mu W/cm^2$ light intensity.

Dehalogenation of kepone (Dawson, et al., 1978, in Dawson, et al., 1980) and enhanced PBB (Christensen and Weimer 1979) photolysis have been reported when hydrogen donors in the form of amino groups have been added to contaminated soils prior to irradiation with sunlight. However, no observable degradation of PCBs in soil was found with amine-enhanced soil (Meuser and Weimer, 1982).

Soil photodecomposition of PCBs was reported by Occhiucci and Patacchuiola, (1982) and was shown to be enhanced by the addition of a proton donor, triethylamine, to the waste/montmorillonite system. Addition of triethylamine resulted in a 2.5 to 5-fold increase in PCB degradation over a 100 hour irradiation period, providing 4 to 18 percent decomposition of the various chlorinated species tested.

The dechlorination reactions described above result from hydrogen abstraction by organic radicals formed upon irradiation as presented by Bunce (1982). Optimization of this process for soil systems has yet to be accomplished but appears to represent an area of potential for use in the in-place treatment of stable, nonmobile compounds.

Activated carbon adsorption of organics at hazardous waste sites followed by chemical addition and photolysis has been reported by React Environmental Crisis Engineers, St. Louis, MO (personal communication, 1983). The site is impregnated with activated carbon and soils are sampled. The most highly contaminated materials are physically removed, packaged, and disposed of in an approved hazardous waste disposal facility. The remaining material is mixed with sodium bicarbonate to increase soil pH, and the material is allowed to photochemically react resulting in the photolysis of the parent material. The level of treatment is expected to be high to medium. An increase in soil pH is the major secondary impact of the treatment method.

Wastes Amenable to Treatment

Photodegradable organic wastes are amenable to this treatment. Generally, this includes compounds with moderate to strong absorption in the >290-nm wavelength range. Such compounds generally have an extended conjugated hydrocarbon system or a functional group with an unsaturated hetero atom (e.g., carbonyl, azo, nitro). Groups that typically do not undergo direct photolysis include saturated aliphatics, alcohols, ethers, and amines. Tetrachlorodibenz-p-dioxin (TCDD), kepone, and PCBs have been treated with this method.

Status of Technology

In the field, several hazardous waste sites have been treated by this method. Laboratory studies have demonstrated the potential for photo-oxidation. However, the potential for the production of hazardous compounds from photodegradation needs to be further researched.

Ease of Application

Materials which are hydrogen donors are applied and depending on the depth of contamination, the soil is tilled to expose waste to the light. This may be easy or difficult depending on the trafficability of the site and the depth of contamination. Runon and runoff controls may be necessary to manage the drainage and erosion.

Potential Achievable Level of Treatment

The level of treatment achievable is potentially high, based on limited experimental data. Effectiveness also depends on the amount of tillage possible at the site and the depth of contamination.

Reliability of Method

Considering that hazardous compounds may be produced as a consequence of photodegradation, unless the constituents in the wastes and their photodegradation products are known, this is not a reliable method.

Secondary Impacts

Production of hazardous compounds from the photodegradation of pesticides has been documented, e.g., dieldrin formation from aldrin, paraoxon formation from parathion, phosgene formation from chloropicrin (Crosby 1971), and the formation of PCBs from the photoreaction of DDT (Woodrow et al., 1983). The potential for such occurrences with additional parent compounds is expected to be high and further research is needed to identify potential toxic product formation to ensure the safe application of this treatment methodology.

Equipment and Exogenous Reagents

Power implements, tillers, and applicators are required to apply the proton donors.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- absorption spectra of waste constituents (at wavelength >290 nm, molecular absorptivities, absorption maxima, quantum yield);
- photolysis rate constant(s);
- products of photolysis (particularly hazardous products);
- volatility of organics (vapor pressure, Henry's Law Constant);

- depth, profile, and areal distribution of contamination;
- light intensity at site;
- trafficability of soil and site.

Sources of Information

Cupitt, 1980; Lemaire, et al., 1981; Spencer, 1980; Nilles and Zabik, 1975; Hautala, 1978; Burkhard and Guth, 1979; Crosby, 1971; Plimmer, 1971; Klopffer, 1980; Sims and Overcash, 1983; Plummer, 1973; Wiff, 1978; Liberte, et al., 1978; Dawson, et al., 1980; Christensen and Weimer, 1979; Meuser and Wiemer, 1982; Occhiucci and Patacchiola, 1982; Bunce, 1982; Woodrow, et al., 1983; Hendry and Kenley, 1979; Graedel, 1978.

3.4.3.2 Enhancement of Volatilization

Description

Enhancing volatilization of compounds from the soil which are susceptible to photodegradation may be a potential treatment technique. This method involves increasing the bulk density or drying of the soil system to increase soil vapor pore spaces and subsequently increase the vaporization rate of desired compounds, followed by photodegradation in air.

Wastes Amenable to Treatment

The technique is applicable to compounds of low water solubility, with low K_D values, low K_W values, and those that are highly photoreactive and that, once within the lower atmosphere, would have a relatively short half life (on the order of hours or preferably minutes). Generally, this includes compounds with moderate to strong absorption in the >290-nm wavelength range. Such compounds generally have an extended conjugated hydrocarbon system or a functional group with an unsaturated hetero-atom (e.g., carbonyl, azo, nitro). Groups that typically do not undergo direct photolysis include saturated aliphatics, alcohols, ethers, and amines.

Status of Technology

This technology is conceptual, based on observed laboratory reaction rates for waste constituents in simulated atmospheres. No information concerning the enhancement of volatilization to increase photolysis has been reported in the literature either on laboratory or pilot scale. Theoretically the process can be expected to be effective for compounds of high volatility and high photoreactivity. Further investigations concerning this process are needed.

Ease of Application

The soil may be tilled to enhance vaporization. Drying of the soil to increase volatilization may be accomplished by tilling, or by installation of a drainage system. This technology may be easy or difficult to apply, depending on the trafficability of the site and the depth of contamination. Controls for runon and runoff management may be necessary.

Potential Achievable Level of Treatment

The level of treatment achievable is potentially high for volatile, photoreactive compounds with short atmospheric half-lives.

Reliability of Method

As with the previous treatment technology, hazardous products may result from photodegradation. Unless there is sufficient certainty that the constituents in a waste will not produce hazardous photodegradative products, this technology should not be used.

Secondary Impacts

There is evidence of the production of degradation products that are hazardous from several pesticides. Potentially, this could also be true of other compounds. Tillage used to dry the soil could increase the susceptibility of the site to eorsion.

Equipment and Exogenous Reagents

Power implements, tillers, and a drainage system are required for this treatment technology.

Information Requirements

A determination of the volatility potential of the compounds of concern through an analysis of their partition coefficients, along with a determination of their half lives, will allow a determination of the applicability of this proposed treatment technique to a specific situation. The information requirements are:

- characterization and concentration of wastes, particularly organics at site;
- absorption spectra of waste constituents (at wavelengths >270 nm, molar absorptivities, absorption maxima, quantum yield);
- photolysis rate constant(s);
- products of photolysis (particularly hazardous products);
- volatility of organics (vapor pressure, Henry's Law Constant);
- depth, profile, and areal distribution of contamination;
- soil moisture;
- light intensity at site;
- trafficability of soil and site.

Sources of Information

Burkhard and Guth, 1979; Crosby, 1971; Crosby, et al., 1971; Cupitt, 1980; Hautala, 1978; Klopffer, 1980; Lemaire, et al., 1982; Nilles and Zabik, 1975; Plimmer, 1971; Sims and Overcash, 1983.

3.5 ATTENUATION

The basic principle of attenuation is the mixing of contaminated soil (or wastes) with clean soil to reduce the concentrations of hazardous components to acceptable levels. This process is potentially applicable to both inorganics and organics. However, acceptable concentration limits have been established only for heavy metals.

3.5.1 Attenuation of Metals

Description

Attenuation of metals which accumulate at the soil surface may be accomplished by either mixing subsurface soil with the top soil, or by applying uncontaminated soil from the adjacent area. Soil may also be purchased from local contractors, or pure soil materials (e.g., bentonite) may be obtained from commercial suppliers.

The treatment requires no chemical additives and is good for large-scale contaminated areas. It can easily be used with other treatments, such as pH adjustment, to maximize metal sorption to soils, to enhance its effectiveness. However, attenuation is generally not applicable for contamination below the plow layer (about 2 feet).

Wastes Amenable to Treatment

This treatment is applicable to all kinds of wastes containing metals. It is particularly applicable to wastes for which concentrations in soil have been defined. For those wastes which are extremely toxic, destructive treatment might be more acceptable.

Status of Technology

This technology has been applied in land treatment systems in which the addition of wastes to soil is controlled and monitored.

Ease of Application

Attenuation for metals may be easy or difficult to apply depending on site/soil trafficability considerations and depth of contamination. Thorough mixing is required. The site should be evaluated for erosion potential, and erosion controls and provisions for containment and treatment of runoff instituted as necessary. Controis for the prevention of runon of precipitation (both surface and subsurface) may also be necessary.

Potential Achievable Level of Treatment

The level of attenuation achievable depends primarily on the concentration and depth of contamination. It could be high with appropriate site/soil trafficability and if the contamination is not deep into the ground.

Reliability of Method

This method is reliable. However, the mixing of soil or addition of other soil into the site may alter the properties of the natural soil. Because of the increased mobility of metals with decreased pH, liming and reliming of the site may be necessary to maintain the metals in the soil if the pH is altered due to the treatment.

Secondary Impacts

The mixing of the soil profile or the addition of different soil may alter the physical, chemical, and biological properties of the original soil at the site. This may have adverse effects. Tilled soils are also usually more susceptible to water and wind erosion.

Equipment and Exogenous Reagents

Power implements and tillers are necessary. If new material is added, applicators will be necessary. Liming material and soil may also be needed.

Information Requirements

- characterization and concentration of metals in waste;
- depth, profile, and areal distribution of contamination;
- soil assimilative capacity of metals, both contaminated and uncontaminated soils;
- soil pH;
- trafficability of soil and site.

3.5.2 Attenuation of Organics

Description

Attenuation of organics in soil is performed in the same manner as attenuation for inorganics discussed above. In addition, the potential for a higher percentage of sorbed organics with an increased mass of soil may increase the level of attenuation for organics. The Freundlich Isotherm used to describe sorption is discussed under Immobilzation (Section 3.3).

As the amount sorbed per unit dry mass of soil (S in Equation 3.1) decreases, the percent sorbed increases. Therefore, the incorporation by mixing of endogenous soil layers, or the addition of exogenous soil to contaminated soil, represents another technology to increase the extent and effectiveness of immobilization of chemical contaminants at hazardous waste sites, and may also aid in decreasing toxicity of the contaminated soil to soil micro-organisms that is due to high concentrations of constituents.

Wastes Amenable to Treatment

This treatment is applicable to all organic wastes. However, organics that are very soluble in water may be more effectively treated by other methods since large amounts of soil may be required to reduce the mobility of the compound. If very toxic components are present in the waste, destructive treatment would be the preferable treatment alternative.

Status of Technology

There is limited field experience in this technology. Addition of dry soils for accomplishing treatment has been utilized for PCB wastes. Waste oil pits, that held transformer fluid containing PCB's ruptured causing a release of 740,000 liters of oil and acidic water. After dewatering, the oils remaining in the pits were treated by the addition of dry soil (Eckenfelder, 1970).

Ease of Application

The endogenous soil profile is tilled to mix uncontaminated soil with the contaminated layers. If the desired attenuation is not reached, imported soil or clay may be applied. This method may be easy or difficult depending on site/soil trafficability considerations for tillage and incorporation of added soil or clay. Erosion may be a problem due to tillage. Controls for erosion prevention and containment and runoff treatment may be necessary. Controls for ri prevention of runon of precipitation (both surface and/or subsurface) may also be necessary.

Potential Achievable Level of Treatment

The level of attenuation achievable is potentially high with suitable size, soil, and waste characteristics.

Reliability of Method

The mixing of soil or addition of other soil or clay to the soil system may alter the properties of the natural soil. As a result, the effectiveness of this method may vary for different compounds, and may not be as expected. However, this method should be reliable under most conditions.

Secondary Impacts

Toxic concentrations to soil organisms may be reduced and biodegradation may be enhanced by this treatment. If clay is added, clay catalyzed degradation and ion-exchange in the clay surface may also be enhanced. However, the mixing of the soil profile or the addition of different soil may alter the physical, chemical, and biological properties of the original soil at the site adversely. Tilled soils are usually more susceptible to water and wind erosion.

Equipment and Exogenous Reagents

Power implements and tillers are necessary. Applicators will be necessary for the addition of new soil or clay.

Information Requirements

- characterization and concentration of organic waste constituents;
- depth, profile, and areal distribution of contamination;
- soil organic carbon content;
- soil moisture;
- trafficability of soil and site.

Sources of Information

Eckenfelder, Jr., 1970.

3.6 REDUCTION OF VOLATILIZATION

Volatilization from a hazardous waste site may need to be controlled to reduce air emissions or to retain compounds within the soil system longer to allow for in-place treatment. There are three ways to reduce volatilization from a site: reduction of soil vapor pore volume, use of physical/chemical barriers, and soil cooling.

3.6.1 Reduction of Soil Vapor Pore Volume

Description

Reduction of soil vapor pore volume for volatilization control is accomplished by modifying the soil system to reduce the partitioning of a compound into the vapor phase and subsequently reduce its rate of volatilization. Such modifications include compaction and water addition to reduce the air-filled pore spaces within the soil. These techniques are especially applicable to those compounds found to represent a high vapor phase mobility potential and a low water phase partition potential (i.e., for compounds with a K_D x K_W product greater than about 50, and a K_D value greater than 10, where K_D is the soil:water partition coefficient and K_W is the air:water partition coefficient).

Under these circumstances, addition of moisture does not materially decrease the percent sorbed to the soil surface, but reduces greatly the soil vapor pore spaces. Air filled porosity is the soil parameter of major significance affecting volatilization because of increased partitioning onto the soil from the soil vapor phase as the volume of the vapor phase is reduced due to soil compaction and/or water addition (Farmer, et al., 1980).

Evaluation of the effectiveness of soil modifications on contaminant loss via vapor movement can be made rapidly using the technique described by Farmer et al. (1980), assuming steady-state vapor flux through a soil cover, i.e.:

$$J = - D_s (C - C_s)/L \qquad (3\text{-}17)$$

where

J = vapor flux (ng/cm^2/d),

D_s = apparent steady-state diffusion coefficient (cm^2/d),

C = concentration in the air at the soil surface (ng/cm^3),

C_s = concentration in the air at the bottom of the soil layer, i.e., saturation vapor pressure assuming steady-state (ng/cm^3),

L = depth of the soil layer, cm.

Millington and Quirk (1961) have suggested the use of the following equation for apparent diffusion in soil taking into account the porosity of the soil:

$$D_s = D_o (P_a{}^{10/3}/P_T{}^2) \tag{3-18}$$

where:

D_o = diffusion coefficient in air (cm^2/d),

P_a = soil air filled porosity, (cm^3/cm^3),

P_T = total soil porosity (cm^3/cm^3), 1 — soil bulk density/particle density,

θ = volumetric water content (cm^3/cm^3),

while Thibodeaux and Hwang (1982) model apparent soil diffusion using total soil porosity and tortuosity:

$$D_S = D_o P_T/t \tag{3-19}$$

where

t = soil tortuosity.

Equation (3-17) then becomes:

$$J = -D_o (P_a{}^{10/3}/P_T{}^2)(C - C_s)/L \tag{3-20}$$

or:

$$J = -D_o (P_T/t)(C - C_s)/L \tag{3-21}$$

Using oxygen as a reference, diffusion coefficients of other compounds can be estimated using:

$$D_A = 0.178 \text{ cm}^2/\text{s} \, (32/M_A)^{0.5} \tag{3-22}$$

where:

D_A = air diffusion coefficient for compound A (cm^2/s) in air at 0°C

M_A = molecular weight of compound A (μg/mole)

Temperature corrections are made to the above value according to:

$$D_{A2} = D_{A1}(T_2/T_1)^{0.5} \tag{3-23}$$

where:

D_{A1}, D_{A2} = diffusion coefficients at temperatures T_1 and T_2, respectively.

A compound's saturation concentration, C_s, may be calculated using the following relationship:

$$Cs = pM/RT \tag{3-24}$$

where:

p = compound vapor pressure (mm Hg),

M = compound molecular weight (μg/mole),

R = universal gas constant (L mm Hg/°K mole),

T = absolute temperature (°K).

Laboratory evaluation of hexachlorobenzene (HCB) vaporization from simulated landfill areas has been reported by Farmer et al. (1980). They found that increases in soil moisture content produced logarithmic decreases in HCB vaporation (an increase in θ from 17.24 to 19.58 percent resulted in HCB flux reductions of 20 percent). Water phase mobility of HCB was not of concern due to HCB's water solubility of only 6.2 $\mu g/l$.

Bulk density effects were also shown by Farmer, et al. (1980) to have a large impact on HCB vapor movement. An increase in bulk density from 0.96 to 1.15 g/cm^3 resulted in a 65 percent reduction in HCB flux from the laboratory landfill units.

Because of the insoluble nature of HCB, its volatilization flux through a water layer was shown to be reduced by a factor of 870 as compared to uncovered samples (Farmer, et al., 1980). Farmer, et al. indicated an expected similar reduction in HCB vapor flux to take place upon saturation of contaminated soil systems. Similar results would be expected for compounds with properties similar to those of HCB. Leaching would be minimized due to the low water solubility and the slight compound partitioning into the soil water phase.

Wastes Amenable to Treatment

This treatment is useful for most volatile organic (e.g., benzene, gasoline, phenol) and inorganic (e.g., H_2S, NH_3, Ra, methyl mercury) compounds. The nature of the waste is also very important. As discussed earlier, these control technologies are especially applicable to those compounds with a high vapor phase mobility potential and a low water phase partition potential.

Status of Technology

Reduction of soil vapor pore volume is at the laboratory stage for uncontrolled hazardous waste sites. Decreases in volatilization of compounds due to water addition and increase in bulk density have been demonstrated from simulated landfill areas.

Ease of Application

Irrigation water is applied to reduce vapor-filled pore space, but not in such amounts that would cause leaching of hazardous constituents. Frequent smaller applications are more desirable. This is comparatively easy. Soil may be compacted to increase bulk density so vapor-filled pore space is reduced.

Potential Achievable Level of Treatment

The achievable level of treatment is potentially low to medium, depending on the waste characteristics. This technology is most effective for constituents with a high vapor phase potential and a low water phase partition potential. The achievable level of treatment also depends on site and soil conditions that are necessary for the addition of soil moisture and for compaction to increase bulk density of the soil.

Reliability of Method

Since soil moisture evaporates, retreatment with irrigation water from time to time is essential for effective reduction in volatilization.

Secondary Impacts

There is a potential for increased liquid phase mobility when water is used if the constituent has a high K_w and low K_{oc}, i.e., it readily partitions into the water phase and is highly water-soluble. Compaction reduces aeration in the soil and could adversely affect degradative reactions, e.g., chemical oxidation or aerobic biodegradation. Similarly, reducing pore volume with increasing soil moisture content would reduce oxygen content.

Equipment and Exogenous Reagents

Irrigation and compaction equipment are required. Irrigation water is the reagent used in this technology.

Information Requirements

- characterization and concentration of waste, primarily organics at site;
- volatility of organic constituents (vapor pressure, Henry's Law Constant, air/water partition coefficient, solubility);
- sorption of organics in soil (K_{oc});
- depth, profile, and areal distribution of contamination;
- bulk density, particle density, tortuosity of soil pores, temperature, and organic matter content of soil;
- soil moisture content;
- precipitation at site;
- trafficability of soil and site.

Contaminant K_W and K_D or K_{OC} estimates will provide information necessary to indicate the relative importance of vapor and solution phase transport and will dictate appropriate control methods for the compounds.

Sources of Information

Farmer, et al., 1980; Millington and Quirk, 1961; Thibodeaux, and Hwang, (1982).

3.6.2 Soil Cooling

Description

Soil cooling may be used to decrease the temperature of soil systems to reduce the vapor pressure of volatile constituents and correspondingly reduce their volatilization rate. The technique may enhance treatment by other means through the retention of compounds for longer periods of time within the soil system.

One means of lowering soil temperature is by the use of cooling agents applied to the soil surface. Greer, and Gross, (1980) found solid carbon dioxide (dry ice) to be more effective than liquid carbon dioxide, liquid nitrogen, or ice in reducing ethyl ether vaporization from a liquid pool. They observed ethyl ether vapor concentration reductions from 8300 to 96 ppm with dry ice addition. Dry ice resulted in a liquid pool temperature of −85°C for 80 minutes at an application rate of 250 kg/2.7 m^3. Liquid nitrogen produced −120°C temperatures but required 1025 kg to reduce concentrations from 93,000 to 116 ppm, and was found more difficult to work with than the dry ice. Because of the effectiveness of solid carbon dioxide and its minimal risks for response personnel during its application, it was the cooling agent of choice (Greer and Gross, 1980).

Modifications to the soil surface may also result in cooler soil temperatures (Baver, et al., 1972). Vegetated soils are usually cooler in the summer but warmer in the winter. Soils with more moisture warm up more slowly in the spring. Irrigation can be used for cooling in the summer. Tillage of the soil creates a surface barrier reducing heat flow from the surface to the subsurface. Mulched soils are cooler in spring, winter, and fall, while summer temperatures are similar between mulched and bare plots.

Soil temperature control is discussed in greater detail in Section 4.

Wastes Amenable to Treatment

Volatile organics are the most suitable wastes for this technology.

Status of Technology

Experimental and limited field applications of cooling agents have been conducted only on liquid spills, and no reports are available on soil surface cooling for vapor mitigation. Soil cooling by soil surface modification is used in agricultural operations.

Ease of Application

Cooling agents are continually applied to soil surface with spray equipment for liquefied agents or with grinding and spreading equipment for solid agents. Mulch is applied by standard agricultural methods. Water is applied at frequent intervals through irrigation systems in small amounts. The use of cooling agents would be difficult due to the low temperature and the reactions that occur upon application of low-temperature materials. Soil modifications using mulches, tilling, and other techniques vary in difficulty depending on trafficability considerations.

Potential Achievable Level of Treatment

The effectiveness of soil cooling is related to the degree of temperature reduction possible. Cooling agents are more effective than soil modifications, but are not likely to be practical because of cost.

Reliability of Method

Soil modification techniques are more reliable than cooling agents. The latter would not be reliable for large areas or for long periods of time, and the extremely low temperatures obtainable would be unnecessary. Retreatment of soil surface modification techniques is necessary.

Secondary Impacts

Low temperatures may decrease or inhibit microbial activity. Extremely low temperatures may severely decrease microbial numbers and/or activity. The application of excessive irrigation water may result in leaching of hazardous constituents. Tilling will increase the potential for erosion at the site and actually increase the surface area available for volatilization.

Equipment and Exogenous Reagents

Mulch, applicators, grinders, tillers, and cooling agents are needed for the technology.

Information Requirements

- characterization and concentration of wastes, particularly organics at site;
- volatility of organic constituents (vapor pressure, Henry's Law Constant, air/water partition coefficient, solubility, and particularly their dependence on temperature);
- sorption of organics in soil (K_{oc});
- depth, profile, and areal distribution of contamination;
- soil moisture;
- effectiveness of cooling agents;
- trafficability of soil and site.

Sources of Information

Green and Soors, 1980; Baver, et al., 1972.

SECTION 4
MODIFICATION OF SOIL PROPERTIES

4.1 INTRODUCTION

Implementation of in-place treatment techniques for contaminated soils often involves the modification of soil properties. Biological degradation, for example, can be enhanced by the addition of nutrients, and immobilization of heavy metals may require adjustment of soil pH. Soil properties discussed in this section include:

- oxygen content,
- moisture content,
- nutrient content,
- pH,
- temperature.

This Section emphasizes the mechanics of soil property modification, independent of the treatment technology. Table 4-1 lists the technologies of Section 3, indicating which soil properties may require modification as a part of treatment.

4.2 CONTROL OF OXYGEN CONTENT

Oxygen content in surface soils can be increased primarily through the use of tillage equipment which breaks, mixes and aerates the soil. Alternatively, oxygen content can be decreased by compaction or increased moisture content. Aeration of subsurface soils not accessible to tillage equipment can be accomplished using construction equipment, such as a backhoe, or using a well point injection system.

A variety of equipment is available to aerate surface soils. This equipment, grouped under the category of Tillers, is described in the appendix. Tilling equipment can also be used to mix wastes or reagents into the soil. Choice of equipment depends on the amount of soil disturbance or mixing desired, and on site characteristics such as the rockiness of the soil.

For some processes, such as anaerobic biological degradation, surface soil compaction may be desirable. By reducing pore sizes and restricting reaeration, anaerobic microsite frequency in the soil will increase. Compaction helps draw moisture to the soil surface. Thus, the problems of leaching that may occur if anaerobiosis were achieved by water addition would be lessened. If the compaction itself were not adequate to achieve the required degree of anaerobiosis, water could be added. Less water, however, should be required in a compacted soil than in an uncompacted soil; thereby minimizing the leaching potential. Volatilization may also be suppressed by surface soil compaction.

Aeration of soils deeper than about 2 feet can be accomplished by air injection through well points. In one case, air was injected into a series of 10 wells using diffusers attached to paint sprayer-type compressors. They delivered about 2.5 cfm to enhance microbial degradation. Various nutrients were added simultaneously. The diffusers were positioned 5 feet from the bottom of the well and below the water table (Raymond, et al., 1976). Aeration through well points has been primarily used for saturated soils and has been shown to be effective. Applicability of the technique for unsaturated soils is not certain.

TABLE 4-1. SOIL MODIFICATION REQUIREMENTS FOR TREATMENT TECHNOLOGIES

Technology	Oxygen Content	Moisture Content	Nutrient Content	pH	Temperature
EXTRACTION	–	–	–	X	X
IMMOBILIZATION					
Sorption (heavy metals)					
Agri. products	–	–	–	X	–
Activated carbon	–	–	–	X	–
Tetren	–	–	–	X	–
Sorption (organics)					
Soil moisture	–	X	–	–	–
Agri. products	–	–	–	–	–
Activated carbon	–	–	–	–	–
Ion exchange					
Clay	–	–	–	X	–
Synthetic resins	–	–	–	X	–
Zeolites	–	–	–	X	–
Precipitation					
Sulfides	X	X	–	X	–
Carbonates, phosphates and hydroxides	X	X	–	X	–
DEGRADATION					
Oxidation					
Soil-catalyzed reactions	X	–	–	X	–
Oxidizing agents	X	–	–	X	–
Reduction					
Reducing agents	X	X	–	X	–
Chromium	X	–	–	X	–
Selenium	X	–	–	X	–
PCBs and Dioxins	–	X	–	–	X
Polymerization	–	–	–	–	–
Modification of soil properties (for biodegradation)					
Soil moisture	–	X	–	–	–
Soil oxygen – aerobic	X	–	–	–	–
Soil oxygen – anaerobic	X	X	–	–	–
Soil pH	–	–	–	X	–
Nutrients	–	–	X	–	–
Nonspecific org. amendments	–	–	–	–	X
Analog enrichment for cometabolism	–	–	–	–	X
Exogenous acclimated or mutant micro-organism	–	–	X	–	X

(continued)

TABLE 4-1 (Continued)

Technology	Oxygen Content	Moisture Content	Nutrient Content	pH	Temperature
Cell-free enzymes	–	–	–	–	X
Photolysis					
Proton donors	–	–	–	–	–
Enhance volatilization	–	X	–	–	–
ATTENUATION					
Metals	–	–	–	–	–
Organics	–	–	–	–	–
REDUCTION OF VOLATILES					
Soil Vapor Volume	–	X	–	–	–
Soil Cooling	–	–	–	–	X

Source: Arthur D. Little, Inc.

4.3 MOISTURE CONTROL

Control of moisture content of soils at an in-place treatment site may be essential for control and optimization of some degradative and sorptive processes as well as for suppression of volatilization of some hazardous constituents. Moisture control may take the form of supplemental water to the site (irrigation), removal of excess water (drainage, well points), a combination of techniques for greater moisture control, or other methods, such as soil additives.

4.3.1 Irrigation

Irrigation may be accomplished by subirrigation, surface irrigation, or overhead (sprinkler) irrigation (Fry and Grey, 1971).

With subirrigation, water is applied below the ground surface and moves upward by capillary action. If the water has high salinity, salts may accumulate in the surface soil, resulting in an adverse effect on soil microbiological activity. The site must be nearly level and smooth, with either a natural or perched water table, which can be maintained at a desired elevation. The groundwater is regulated by check dams and gates in open ditches, or jointed perforated pipe to maintain the water level in soil. The use of such systems is limited by the restrictive site criteria. There may be situations in which a subirrigation system may be combined with a drainage system to optimize soil moisture content. However, at a hazardous waste site, raising the water table might result in undesirable groundwater contamination.

Trickle irrigation is a system of supplying filtered water directly on or below the soil surface through an extensive pipe network with low flow-rate outlets only to areas which require irrigation. It does not give uniform coverage to an area, but with proper management, does reduce percolation and evaporation losses. For most in-place treatment sites, this method would probably not be appropriate, but it may find application in an area where only "hot spots" of wastes are being treated.

Surface irrigation includes flood, furrow, or corrugation irrigation. Since the prevention of off-site migration of hazardous constituents to ground or surface waters is a primary restraint on in-place treatment technology, the use of surface irrigation should be viewed with caution. Contaminated water may also present a hazard to on-site personnel.

In flood irrigation, water covers the surface of a soil in a continuous sheet. Theoretically, water should stay at every point just long enough to apply the desired amount, but this is difficult or impossible to achieve under field conditions.

In furrow irrigation, water is applied in narrow channels or furrows. As the water runs down the furrow, part of it infiltrates the soil. Considerable lateral movement of the water is required to irrigate the soil between furrows. Salts also tend to accumulate in the area between furrows. Furrow irrigation frequently requires extensive land preparation, which usually would not be possible or desirable at a hazardous waste site due to contamination and safety considerations.

In corrugation irrigation, as with furrow irrigation, water is applied in small furrows from a head ditch. However, in this case, the furrows are used only to guide the water, and overflooding of the furrows can occur.

In general, control and uniform application of water is difficult with surface irrigation. Also, soils high in clay content tend to seal when water floods the surface, limiting water infiltration.

The basic sprinkler irrigation system consists of a pump to move water from the source to the site, a pipe or pipes leading from the pump to the sprinkler heads, and the spray nozzles. Sprinkler irrigation has many advantages. Erosion and runoff of irrigation water can be controlled or eliminated, application rates can be adjusted for soils of different textures, even within the same area, and water can be distributed more uniformly. Irrigation is also possible on steep, sloping land and irregular terrain. Usually less water is required than with surface flooding methods, and the amount of water applied can be controlled to meet the needs of the in-place treatment technique.

There are several types of sprinkler irrigation systems:

1) Permanent installations with buried main and lateral lines;

2) Semi-permanent systems with fixed main lines and portable laterals;

3) Fully portable systems with portable main lines and laterals, as well as a portable pumping plant.

The first two types (especially the first) would likely not be appropriate nor cost-effective for a hazardous waste site because of the required land disturbance for installation and the limited time period for execution of the treatment.

The fully portable systems may have hand-moved or mechanically moved laterals. To eliminate movement by hand, the system may have enough laterals to cover the whole area (a solid set system). Portable systems can be installed in such areas as forests in patterns such as to avoid interference with trees. Mechanically moved laterals may be divided into three categories: side-roll wheel move; center pivot systems; and traveling sprinklers. The amount of labor is considerably reduced compared to portable systems, but the cost of the equipment is higher. However, the health and safety of workers must be considered as well as cost in the choice of an appropriate system.

The side-roll wheel move is a lateral suspended on a series of wheels. The unit is stationary during operation and is moved while shut off by an engine mounted at the center of the line or an outside power source at one end of the line. A variation of this system is a continuous travel wheel with a flexible hose, which remains in operation as the wheel moves across the field.

The center pivot system is a pipeline suspended above ground with various sized sprinklers spaced along its length. The system is self-propelled and continuously rotates around a pivot point.

The traveling sprinkler consists of a single gun sprinkler mounted on a portable, wheeled unit which is self-propelled up and down the length of the field.

The choice of an appropriate irrigation system depends on site conditions, costs, and health and safety considerations for both on-site personnel and off-site populations. The system should be designed by a qualified specialist such as an agricultural engineer. Preliminary guidelines for designing an irrigation system can be found in the *Sprinkler Irrigation Handbook* (Fry and Grey, 1971) and *Planning for an Irrigation System* (Turner and Anderson, 1980). The latter publication, in addition to technical aspects of irrigation, also discusses sources of water, including legal rights, and methods of determining irrigation costs.

4.3.2 Drainage

A properly designed drainage system removes excess water and/or lowers the groundwater level to prevent waterlogging. Surface drainage is accomplished by open ditches and lateral drains, while subsurface drainage is accomplished by a system of open ditches and buried tube drains into which water seeps by gravity. The collected water is conveyed to a suitable disposal point. Subsurface drainage may also be accomplished by pumping from wells to lower the water table. Caution is required at a hazardous waste site to ensure that drainage water disposed off-site is not contaminated with hazardous substances. Provisions must be made to collect, store, treat, and/or recycle water that is not acceptable for off-site release. The drainage system should be managed to prevent or minimize contamination problems.

The design of a drainage system is affected by the topography, soil properties, and water source factors of a site. The two types of drainage systems are (Donnan and Schwab, 1974):

- surface drains — used where subsurface drainage is impractical (e.g., impermeable soils, excavation difficult), to remove surface water or lower water table;

- subsurface drains — used to lower the water table. Construction materials include clay or concrete tile, corrugated metal pipe, and plastic tubing. Selection depends on strength requirements, chemical compatibility, and cost considerations.

For the design and construction of a drainage system, a drainage engineer should be consulted. The American Society of Agronomy monograph, *Drainage for Agriculture* (Schilfgaarde, 1974) contains a complete discussion of drainage.

4.3.3 Well Points

Well points, like subsurface drains, can be used to lower the water table in shallow aquifers. They typically consist of a series of riser pipes screened at the bottom and connected to a common header pipe and centrifugal pump. Well point systems are practical up to 10 meters (33 feet) and are most effective at 4.5 meters (15 feet). Their effectiveness, however, depends on site-specific conditions, such as the horizontal and vertical hydraulic conductivity of the aquifer (Ehrenfeld and Bass, 1983).

4.3.4 Additives

Various additives are available to enhance moisture control. For example, the water-retaining capacity of the soil can be enhanced by adding water-storing substances. Three such synthetic substances were recently evaluated by Nimah, et al. (1983) for use in arid area soils. They found that available soil water content was increased by two of the products. Water-repelling agents are available which diminish water absorption by soils. On the other hand, water-repelling soils can be treated with surface-active wetting agents to improve water infiltration and percolation. Other soil characteristics which have been modified by surface active agents include acceleration of soil drainage, modification of soil structure, dispersion of clays, and soil made more compactable. Evaporation retardants are also available to retain moisture in a soil. Secondary effects of some of these amendments on soil biological activities, other soil physical properties, soil chemical properties and environmental effects, e.g., leachability and degradability, are discussed by Brandt, G.H., (1972).

4.4 NUTRIENT ADDITIONS TO THE SOIL

Degradation of organic compounds at a hazardous waste site requires an active population of micro-organisms. Among other environmetnal factors (e.g., temperature, moisture, pH, etc.), adequate nutrition is vital to maintain the microbial population at an optimum level. The hazardous wastes being degraded may contribute some necessary nutrients, but may not supply all that are required or that may be beneficial (e.g., silicon and sodium). If the soil does not contain an adequate supply of nutrients, the soil must be supplied with the appropriate elements in the form of fertilizers. A fertilizer is any substance added to the soil to supply those elements required in plant nutrition (Tisdale and Nelson, 1975).

The number of substances suitable as fertilizers is very large, and their compositions and origins differ considerably. Classification systems incorporating many aspects of fertilizer origin, use, and characteristics are presented in Finck (1982). Because of the variety of possible classifications, the choice of an appropriate fertilizer can be complicated, and an agronomist should be consulted to develop a fertilization plan at a hazardous waste site. A plan may include types and amounts of nutrients, timing and frequency of application, and method of application. The nutrient status of the soil and the nutrient content of the wastes must be determined to formulate an appropriate fertilization plan. Basic textbooks on fertilization include *Soil Fertility and Fertilizers* (Tisdale and Nelson, 1975), *Fertilizers and Fertilization* (Finck, 1982), and *Fertilizers and Soil Amendments* (Follett, et al., 1981).

The development of a fertilization program not only includes the proper selection of fertilizer form and determination of correct fertilizer quantities, but also the selection of an application method. Fertilizers must be transported, stored, and applied so that no chemical or physical changes occur to decrease dispersibility and effectiveness. Improper handing during transportation and storage may result in the creation of safety hazards due to moisture absorption, such as increased flammability, explosiveness, and corrosiveness, or the formation of noxious gases. Improper mixing of fertilizer types before or after application may result in nitrogen losses, immobilization of water-soluble phosphate, or deterioration of distribution properties due to moisture absorption (Finck, 1982).

In agricultural application, fertilizers are either applied evenly over an area or concentrated at given points, such as banded along roots. However, at a hazardous waste site, fertilizer will likely be applied evenly over the whole contaminated area and incorporated by tilling, if necessary. Nutrients can also be injected through well points below the plow layer.

With broadcast fertilization, the fertilizer can be left on the surface or incorporated with a harrow (2 to 3 cm deep), a cultivator (4 to 6 cm deep), or with a plow (a layer at bottom of furrow, e.g., 15 cm deep). The depth of incorporation depends on the solubility of the fertilizer and the desired point of contact in the soil. In general, nitrate fertilizers move freely, while ammonia nitrogen is adsorbed by soil colloids and moves little until converted to nitrate. Potassium is also adsorbed and moves little except in sandy soils. Phosphorus does not move in most soils. Therefore, potassium and phosphorus need to be applied or incorporated to the desired point of use.

4.5 CONTROL OF SOIL pH

Control of soil pH at an in-place hazardous waste treatment site is a critical factor in several treatment techniques (e.g., metal immobilization, optimum microbial activity). The goal of soil pH adjustment in agricultural application usually is to increase the pH to near neutral values, since natural soils tend to be acidic.

The areas of the country in which the need for increasing soil pH is greatest are the humid regions of the East, South, Middle West, and Far West States. In areas where rainfall is low and leaching is minimal, such as parts of the Great Plain States and the arid, irrigated saline-alkali soils of the Southwest, Intermountain, and Far West States, pH adjustment is usually not necessary. Some soils, especially those high in carbonates, do require the pH to be lowered. However, a hazardous waste-contaminated soil may have substances high in pH, thus necessitating soil acidification.

The most common method of controlling pH is liming. Liming is the addition to the soil of any calcium or calcium-and magnesium-containing compound that is capable of reducing acidity (i.e., raising pH). Lime correctly refers only to calcium oxide, but is commonly used to refer to calcium hydroxide, calcium carbonate, calcium-magnesium carbonate, and calcium silicate slags (Tisdale and Nelson, 1975).

The benefits of liming to biological activity are several. At higher pH values, aluminum and manganese are less soluble. Both of these compounds are toxic to most plants. In addition, phosphates and most micro-elements necessary for plant growth (except molybdenum) are more available at higher pH. Microbial activity is greater at or near neutral pH, which enhances mineralization and degradation processes and nitrogen transformations (e.g., nitrogen fixation and nitrification).

A summary of commonly used liming materials is presented in Table 4-2. The choice of a liming material depends upon several factors. Calcitic and dolomitic limestones are the most commonly used materials. To be effective quickly, however, these materials must be ground, because the velocity of reaction is dependent on the surface in contact with the soil. The finer they are ground, the more rapidly they react with the soil. However, a more finely ground limestone product usually contains a mixture of fine and coarse particles in order both to effect a pH change rapidly and still be relatively long-lasting as well as reasonably priced. Many states require that 75 to 100 percent of the limestone pass an 8- to 10-mesh sieve and that 20 to 80 percent pass anywhere from an 8- to 100-mesh sieve (Tisdale and Nelson, 1975). Calcium oxide and calcium hydroxide are manufactured as powders and react quickly.

Other factors to consider in the selection of a limestone are neutralizing value, magnesium content, and cost per ton applied to the land.

Lime requirement for soil pH adjustment is dependent on several soil factors, including soil texture, type of clay, organic matter content, and exchangeable aluminum (Follett, et al., 1981). The buffering capacity of soil reflects the ability of soil components to hold a large number of ions in adsorbed or reserve form. Thus, adsorption or inactivation of H+ ions, or the release of adsorbed ions to neutralize OH- ions provides protection against abrupt changes in pH when acidic or basic constituents are added to soil. Differences among soils in their buffering capcity reflect differences in the soil cation exchange capacities and will directly affect the amount of lime required to adjust soil pH. The amount of lime required is also a function of the depth of incorporation at the site, i.e., volume of soil to be treated. The amount of lime required to effect a pH change in a particular site/soil/waste system is determined by a state experimental or commercial soil testing laboratory in short-term treatability studies or soil-buffer tests (McLean, 1982).

Lime requirements may also be affected by acid precipitation and acid-forming fertilizers. A field study in Connecticut showed that each year the acidity generated by acid precipitation would require 36 kg/ha (32 lb/A) of pure calcium carbonate for neutralization (Frink and Voight, 1976).

Lime is usually applied from a V-shaped truck bed with a spinner-type propeller in the back (Follett, et al., 1981). Uniform spreading is difficult with this equipment, and wind losses can be significant. A more accurate but slower and more costly method is a lime spreader (a covered hopper or conveyor) pulled by a tractor. Limestone does not migrate easily in the soil since it is only slightly soluble, and must be placed where needed. Plowing and/or discing surface-applied lime into the soil may therefore be required.

The application of fluid lime is becoming more popular, especially when mixed with fluid nitrogen fertilizer. The combination results in less trips across the soil, and the lime is available to counteract acidity produced by the nitrogen. Also, limestone has been applied successfully to a pharmaceutical wastewater land treatment facility through a spray irrigation system.

TABLE 4-2. LIMING MATERIALS

Liming Material	Description	Calcium Carbonate Equivalent[a]	Comments
Limestone, calcitic	$CaCO_3$, 100% purity	100	Neutralization value usually between 90-98% because of impurities; pulverized to desired fineness
Limestone, dolomitic	65% $CaCO_3$ + 20% $MGCO_3$, 87% purity[b]	89	Pure dolomite (50% $MgCO_3$ ano 50% $CaCO_3$) has neutralizing value of 109%; pulverized to desired fineness
Limestone, unslaked lime, burned lime, quick lime	CaO, 85% purity	151	Manufactured by roasting calcitic limestone; purity depends on purity of raw materials; white powder, difficult to handle – caustic; quick acting; must be mixed with soil or will harden and cake
Hydrated lime, slaked lime, builder's lime	$Ca(OH)_2$, 85% purity	85	Prepared by hydrating CaO; white powder, caustic, difficult to handle; quickly acting
Marl	$CaCO_3$, 50% purity	50	Soft, unconsolidated deposits of $CaCO_3$, mixed with earth, and usually quite moist
Blast furnace slag	$CaSi_2O_3$	75-90	By-product in manufacture of pig iron; usually contains magnesium
Waste lime products	Extremely variable in composition	?	—

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a. Calcium carbonate equivalent (CCE): neutralizing value compared to pure calcium carbonate, which has a neutralizing value defined as 100.

State laws specify a calcium carbonate equivalent averaging 85%.

Source: Follett, R.H., et al., 1981, Tisdale, S.L., and Nelson, W.L., 1975.

4.6 MODIFICATION OF SOIL TEMPERATURE

Soil temperature is one of the more important factors that controls microbiological activity and the rate of organic matter decomposition. Soil temperature is also important in influencing the rate of volatilization of compounds from soil. Soil temperature can be modified by regulating the oncoming and outgoing radiation, or by changing the thermal properties of the soil (Baver, et al., 1972).

Vegetation plays a significant role in soil temperature because of the insulating properties of plant cover. Bare soil unprotected from the direct rays from the sun becomes very warm during the hottest part of the day, but also loses its heat rapidly during colder seasons.

However, a well-vegetated soil during the summer does not become as warm as a bare soil, and in the winter, the vegetation acts as an insulator to reduce heat lost from the soil. Frost penetration is more rapid and deeper under bare soils than under a vegetative cover.

Mulches can affect soil temperature in several ways. In general mulches reduce diurnal and seasonal fluctuations in soil temperature. In the middle of the summer, there is little difference between mulched and bare plots, but mulched soil is cooler in spring, winter and fall, and warms up more slowly in the spring. Mulches with low thermal conductivities decrease heat flow both into and out of the soil; thus, soil will be cooler during the day and warmer during the night. White paper, plastic, or other types of white mulch increases the reflection of incoming radiation, thus reducing excessive heating during the day. A transparent plastic mulch transmits solar energy to the soil and produces a greenhouse effect. A black paper or plastic mulch adsorbs radiant energy during the day and reduces heat loss at night. Humic substances increase soil temperature by their dark color, which increases the soil's heat adsorption.

The type of mulch required determines the application method. Mulches, in addition to modification of soil temperature, are also used to protect soil surfaces from erosion and to reduce water and sediment runoff, prevent surface compaction or crusting, conserve moisture, and help establish plant cover (Soil Conservation Service, 1979). A summary of mulch materials is presented in Table 4-3. Commercial machines for spraying mulches are available. Hydromulching is a process in which seed, fertilizer, and mulch are applied as a slurry. To apply plastic mulches, equipment which is towed behind a tractor mechanically applies plastic strips which are sealed at the edges with soil. For treatment of large areas, special machines that glue polyethylene strips together are available (Mulder, 1979).

Irrigation increases the heat capacity of the soil, raises the humidity of the air, lowers air temperature over the soil, and increases thermal conductivity, resulting in a reduction of daily soil temperature variations (Baver, et al., 1972). Sprinkle irrigation, for example, has been used for temperature control, specifically frost protection in winter and cooling in summer and for reduction of soil erosion by wind (Schwab, et al., 1981). Drainage decreases the heat capacity, thus raising the soil temperature. Elimination of excess water in spring causes a more rapid temperature increase. The addition of humic substances improves soil structure, thus improving soil drainability, resulting indirectly in increased soil temperature.

Several physical characteristics of the soil surface can be modified to alter soil temperature (Baver, et al., 1972). Compaction of the soil surface increases the density and thus the thermal conductivity. Tillage, on the other hand, creates a surface mulch which reduces heat flow from the surface to the subsurface. The diurnal temperature variation in a cultivated soil is much greater than in an untilled soil. A loosened soil is colder at night and more susceptible to frost.

TABLE 4-3. MULCH MATERIALS

	Organic Materials	Quality	Notes
a.	Small grain straw or tame hay	Undamaged, air dry threshed straw, free of undesirable weed seed	Spread uniformly – at least 1/4 of ground should be visible to avoid smothering seedling. Anchor either during application or immediately after placement to avoid loss by wind or water. Straw anchored in place is excellent on permanent seedings.
b.	Corn stalks chopped or shredded	Air dried, shredded into 8" to 12" lengths	Relative slow to decompose. Resistant to wind blowing.
c.	Wood Excelsior	Burred wood fibers approximately 4" long	A commercial product packaged in 80-90 lbs. bales. Apply with power equipment. Tie down usually.
d.	Wood Cellulose Fiber	Air dry, non-toxic with no growth inhibiting factors	Must be applied with hydraulic seeder.
e.	Compost or manure	Shredded, free of clumps or excessive coarse material	Excellent around shrubs. May create problems with weeds.
f.	Wood chips and bark	Air dried, free from objectionable coarse material	Most effective as mulch around ornamentals, etc. Resistant to wind blowing. May require anchoring with netting to prevent washing or floating off.
g.	Sawdust	Free from objectionable coarse material	More commonly used as a mulch around ornamentals, etc. Requires anchoring on slopes. Tend to crust and shed water.
h.	Pine straw	Air dry. Free of coarse objectionable material	Excellent around plantings. Resistant to wind blowing.

(continued)

TABLE 4-3 (Continued)

	Other Mulch Materials	Quality	Notes
a.	Asphalt Emulsion	Slow setting SS-1	Use as a film on soil surface for temporary protection without seeding. Requires special equipment to apply.
b.	Gravel or Crushed Stone		Apply as a mulch around woody plants. May be used on seeded areas subject to foot traffic. (Approximate weight – 1 ton per cu. yd.)
c.	Wood Excelsior Mats	Blanket of excelsior fibers with a net backing on one side	Roll 36" x 30 yards covers 161/2 sq. yds. Use without additional mulch. Tie down as specified by manufacturer.
d.	Jute, Mesh or Net	Woven jute yarn with 3/4" openings	Roll 48" x 75 yds. weighs 90 lbs. and covers 100 sq. yds.

Source: Soil Conservation Service, 1979.

APPENDIX

COST INFORMATION

TABLE A-1. EQUIPMENT APPLICABLE TO TREATMENT OF HAZARDOUS-WASTE-CONTAMINATED SOILS

Function	Equipment	Principal Use	Examples of Capacity or Size Range	Approximate Cost[a]	Cost Units
Power Implements	Tractors, Crawler	May be needed when maximum traction and stability is needed. Especially useful on steep slopes.	Small, 28 maximum drawbar horsepower	$ 21,800	each
			Large, 300 maximum drawbar horsepower	210,000	each
	Tractors, wheel type, two-wheel drive	Adequate where traction or power requirements are less demanding.	Small, 12 maximum drawbar horsepower	6,000	each
			Large, 164 maximum drawbar horsepower	66,500	each
	Tractors, wheel type four-wheel drive	Better traction and higher horsepower available than with two wheel drive tractors.	Small, 12 maximum drawbar horsepower	6,800	each
			Very large, 552 maximum drawbar horsepower	275,000	each
Tillers: Loosening, aerating, and/or mixing the soil	Plows, Chisel	Loosens and aerates soil to 14 inch depth with minimum vertical mixing.	10 foot width	1,500	each
			41 foot width	18,700	each
	Plows, moldboard	Turn and aerate soil 8 to 12 inches deep. Poor mixing, but useful in rocky soils.	3-bottom, 2-way	4,800	each
	Rotary tillers[b]	Effective verticle mixing and aeration of surface 4 to 10 inches of soil. Combines effects of plowing and cultivation.	40 inch width, 15 inch rotor diameter	1,330	each
			300 inch width, 21 inch rotor diameter	16,600	each
	Subsoilers, chisel	Break up deep soil with little verticle mixing to 30 inches or more.	13 shank, 270 inch width	7,640	each
	Subsoiler, double tilling	Turns surface soil with moldboard plow then loosens and mixes subsoil to 20 inches with a rotary tiller. Fertilizer or other agent can be mixed into the subsoil.			

TABLE A-1. (Continued)

Function	Equipment	Principal Use	Examples of Capacity or Size Range	Approximate Cost[a]	Cost Units
Tillers (Continued)	Harrows, Disc	Loosen and aerate surface soil. Provide more verticle mixing than most other harrows.	Small hitch mounted, 450 lb	450	each
			Large, pull type, 16,700 lb	32,100	each
	Harrows, power	Several varieties of power harrows available which use rotating (verticle or horizontal) oscillating, or reciprocating motion to loosen and aerate surface soil.	Small, 72 inch width, 10 inch working depth	5,000	each
			Large, 240 inch width, 8 inch working depth	19,500	each
	Harrows, spike	Break up clods formed when plowing sticky soil. Loosen and aerate shallow surface soil.	7 foot wide section	160-230	each
	Harrows, spring tooth	Loosen and aerate shallow surface soil, have vibrating action.	8 foot width	940	each
			20 foot width	2,900	each
Compactors: Compacting soil	Rollers	Compact soil surface, improve soil moisture retention, restrict gas diffusion.	4 foot width	586	each
			16 foot width	1,620	each
Applicators: Application of exogenous agent(s)	Sprayers, hydraulic	Treatment with relatively small amounts of fluid agents, e.g., 20 to 200 gallons per acre.	Small, hitch mounted, 7.5-foot treatment width	511	each
			Large, hitch mounted, 60-foot treatment width	9,330	each
			Small, self-propelled, 27-foot treatment width	6,730	each
			Large, self-propelled, 70-foot treatment width	144,000	each
	Spreaders, chemical fertilizer	Apply granular chemical fertilizers or other agents in similar form. Some fertilizer spreaders can be modified to apply agricultural limestone.	Small, hitch mounted 1 to 2 cu ft capacity	214	each
	Spreaders, manure or dried sewage sludge	Apply barnyard manure or dried sewage sludge.	Tractor drawn, 122 cu ft capacity	2,600	each
			Tractor drawn, 391 cu ft capacity	9,490	each
			Truck mounted	Bid	
	Spreaders, agricultural limestone	Apply ground lime or dolomite to soil for pH control.	Small, hitch mounted, 12 cu ft capacity	624	each

TABLE A-1. (Continued)

Function	Equipment	Principal Use	Examples of Capacity or Size Range	Approximate Cost[a]	Cost Units
			Large, truck mounted, 250 cu ft capacity	15,700	each
	Injectors, liquid	Inject liquid materials below the soil surface. Conventional equipment can inject 1100 gal per minute of liquid to 16 inches below the surface.	Self-propelled	Bid	
			Tractor-drawn	Bid	
Grinders: Grind plant Materials	Grinders, tub	Grind hay or similar plant material to be used as organic matter amendment or mulch.	8 ton per hour	12,500	each
			15 to 25 ton per hour	41,000	each
Covers, Mulches: Soil coverings and applicators	Plastic sheeting	Cover soil to manage soil temperature or to suppress volatilization.	2 mil thick 10.5 ft wide, 1400 ft. long	90-95	roll (140 lb)
	Plastic laying machine	Applies plastic sheeting over the soil by unrolling it, buring, and/or gluing the edges. Mounted on tractor hitch.	10.5 ft wide (sizes 9 to 20 ft wide available)	3,300	each
	Hydromulching	Ground plant materials (frequently wood fiber) are sprayed onto the soil in aqueous slurry. Chemical binders may be added to stabilize the material against the wind.		1,500 to 1,700 (Includes mulch, equipment and labor)	pr acre
Irrigation	Sprinkler, hand move	Apply water to manage soil moisture and/or soil temperature. Fertilizers or other treatment agent may be applied with the irrigated water.	Portable, 1 to 40 acres	200-500	pr acre
			Solid set, 1 or more acres	800-2000	pr acre
	Sprinkler, self-move		Motor driven, side roll, 20 to 80 acres	300-500	pr acre
	Sprinker, self-propelled		Center pivot driven by water, 40-240 acres	325-450	pr acre
			Water driven, side roll, 80-160 acres	275-450	pr acre
Drainage	Perforated pipe drains	Lower shallow water table to improve soil aeration.	Costs depend on depths of drains, soil hydraulic conductivity, and site parameters	350-500	pr acre

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a. Manufacturers suggested retail prices are used for most agricultural tractors and implements.

b. Larger rotary tillers can be modified to carry fertilizer or other chemical application equipment so that treatment can be done in a single pass over the soil.

Source: Utah Water Research Laboratory.

TABLE A-2. EXOGENOUS AGENTS, EXCAVATION' AND HAULING COSTS

Identifying Term	Agent	Approximate Cost	Cost[a] Unit
Acidifying Agents	Aluminum sulfate	$235	Ton
	Ferrous sulfate	130	Ton
	Ferric sulfate	108	Ton
	Liquid ammonium sulfide	235	Ton
	Sulfur (crude)	109-126	Ton
	Sulfuric acid	20-96	Ton
Activated Carbon	Activated carbon, powder	0.55	lb
	Activated carbon, granular	1.05	lb
Carbonates/Phosphates	Calcium corbonate (limestone)	6.50-35	Ton
	Triple superphosphate	127-165	Ton
Cooling Agents	Liquid and gas carbon dioxide	0.12	lb
	Liquid nitrogen	0.28	lb
	Solid carbon dioxide	0.16	lb
	Water ice	0.03	lb
Excavation and Hauling	Excavation	0.77-4.58[b] (Average ~ 2.10)	yd^3
	Hauling less than 5 miles	0.50	yd^3-mile
	Hauling more than 5 miles	0.25-0.30	yd^3-mile
Fertilizer	Ammonia, anhydrous	135-180	Ton
	Ammonia, aqueous	210	Ton
	Ammonium nitrate	91-115	Ton
	Ammonium sulfate	74-79	Ton
	Diammonium phosphate	165	Ton
	Phosphoric acid, 52-54%	165	Ton
	Phosphate, rock	23	Ton
	Potassium chloride, 60-62.4%	57	Ton
	Potassium nitrate	277-284	Ton
	Sodium nitrate	130	Ton
	Superphosphate, triple	160-165	Ton
	Urea	200-215	Ton
	Blended fertilizers (N-P-K)		
	16-16-8%	220	Ton
	16-16-16	230	Ton
	18-46-0	260	Ton
	29-14-0	230	Ton
Flushing Agents	Caustic soda, liquid, 50%	150-230	Ton
	Citric acid	0.81	lb
	Hydrochloric acid, 20 Be[c]	55-115	Ton
	Nitric acid, 36°, 38°, 40° Be	195	Ton
	Sodium lauryl sulfate, 30%	0.29-0.32	lb
	Sulfuric acid	20-96	Ton

(Continued)

TABLE A-2. (Continued)

Identifying Term	Agent	Approximate Cost	Cost[a] Unit
Liming Material	Agricultural limestone or dolomite	6.50-34	Ton
	Lime (85% CaO)	31.25-32.50	Ton
	Hydrated lime (85% $CaOH$)	32.50-34.50	Ton
Organic Materials	Animal Tankage	55	Ton
	Alfalfa hay	80-120	Ton
	Bone meal, steamed	300	Ton
	Castor pomace	149	Ton
	Cottonseed meal, 41%	215	Ton
	Horse feed (grains and molasses)	180	Ton
	Manure, dairy cattle	0-1	Cubic Foot
	Molasses	125	Ton
	Peanut meal, 50%	235	Ton
	Sewage sludge, activated	80	Ton
Oxidizing Agents	Hydrogen peroxide, 35-70%	0.22-0.43	lb
	Ozone generator, 22 lb/day	40,000-45,000	Each
	Potassium permanganate	2	Kilogram
Precipitating Agent	Ferrous sulfate	130	Ton
Proton Donors	Methanol	0.48	Gallon
	Mineral oil	2.69-2.72	Gallon
	Vegetable oils	0.22-0.47	lb
	Xylene	1.20-1.60	Gallon
Reducing Agents	Acetic acid	0.23	lb
	Iron powder	1.00	lb
	Soda caustic ($NaOH$-Tech):		
	Liquid, 50%	150-230	Ton
	Flake, 76%	500-570	Ton
	Granular, 75%	520	Ton
	Sodium borohydride powder	18-19	lb
	Sodium borohydride stabilized solution, 12%	16	lb
Resins	Anion Exchange	191-197	Cubic Foot
	Cation exchange	211-217	Cubic Foot
Soil/Clay	Bentonite, industrial grade	94	Ton
	Kaolin, uncalcined	58	Ton
	Top soil	4-10	Cubic Yard

(Continued)

TABLE A-2. (Continued)

Identifying Term	Agent	Approximate Cost	Cost[a] Unit
Sulfides	Ammonium sulfide liquid	235	Ton
	Hydrogen sulfide liquid	0.11	lb
	Sodium sulfide	410-470	Ton
Tetren	Tetraethylenepentamine	1.70-1.78	lb
Zeolites	Clinoptilolite	45-50	Ton

a. Most costs are wholesale, bulk in train car, tank car, or truckload quantities FOB factories or ports.

b. Depends on equipment type and size. Add 60% for hard or rocky soil, deduct 15% in light soil or sand (Godfrey, R.S., ed. 1982. Building construction cost data 1983. Robert Snow Means Co., Inc., Kingston, MA. 421 p.).

c. Be = Baumé.

Source: Utah Water Research Laboratory.

BIBLIOGRAPHY

Ahrens, J.F., and J.B. Kring. 1968. Activated carbon adsorbs pesticides. Front. Plant Sci. 20:13.

Alexander, M. 1977. Introduction to soil microbiology. Second Edition. John Wiley and Sons, New York, NY. 467 p.

Alexander, M. 1981. Biodegradation of chemicals of environmental concern. Science 211:132-138.

American Public Health Association. 1975. Standard Methods for Examination of Water and Wastewater. Fourteenth edition. Wash., D.C.

Anderson, A.H. 1968. The inactivation of simazine and liuron in soil by charcoal. Weed Res. 8:58-60.

Anderson, J.R. 1978. Pesticide effects on non-target soil micro-organisms. pp. 313-533. *In* pesticide microbiology. Hill, I.R. and Wright, S.J.L. (eds.) Academic Press, New York, NY.

Anonymous. 1981. It's hard to find jobs for industrious bugs. Chem. Week 128(2):40-41

Anonymous. 1982. Bugs tame hazardous spills and dumpsites. Chem. Week 130(18):49.

Arthur D. Little, Inc. 1976. State-of-the-art survey of land reclamation technology. EC-CR-76-76. Department of the Army, Edgewood Arsenal, Aberdeen Proving Ground, MD. 105 p.

Artiole, J., and W.H. Fuller. 1979. Effect of crushed limestone barriers on chromium attenuation in soils. J. Environ. Qual. 8:503-510.

Atlas, R.M., and R. Bartha. 1981. Microbial ecology, fundamentals and applications. Addison-Wesley Publishing Company, Reading, MA. 560 p.

Baas Becking, L.G.M., I.R. Kaplan, and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. J. Geology 68:243-284.

Bailey, G.W., J.L. White, and T. Rothberg. 1968. Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. Soil Sci. Soc. Am. Proc. 32:222-234.

Baker, M.D., and C.I. Mayfield, 1980. Microbial and non-biological decomposition of chlorophenols and phenol in soil. Water Air Soil Poll. 13:411-424.

Bartha, R. 1980. Pesticide residues in humus. ASM News 46:356-360.

Baver, L.D., W.H. Gardner, and W.R. Gardner. 1972. Soil physics. Fourth edition. John Wiley and Sons, Inc., New York, NY. 498 p.

Bhattacharyya, D., A.B. Jumawan, G. Sun, C. Sund-Hagelberg, and K. Schwitzgebel. 1981. Precipitation of heavy metals with sodium sulfide: Bench scale and full-scale experimental results. *In* Water-1980, AIChE 209(77).

Biddappa, C.C., M. Chino, and K. Kumazawa. 1982. Migration of heavy metals in two Japanese soils. Plant and Soil 66:299-316.

Black, C.A. (ed.). 1965. Methods of soil analysis. Part 2. Chemical and microbiological properties, Agronomy No. 9, Amer. Soc. Agron. Madison, WI.

Bollag, J.-M. 1983. Cross-coupling of humus constituents and xenobiotic substances. pp. 127-141. *In* Aquatic and terrestrial humic materials. Christman, R.F., and Gjessing, E.T. (eds.). Ann Arbor Science Publishers, Ann Arbor, MI.

Bollag, J.-M., P. Blattman, and T. Laanio. 1978. Adsorption and transformation of four substituted anilines in soil. J. Agric. Food Chem. 26:1302-1306.

Bollag, J.-M., S.-Y. Liu, and R.D. Minard. 1980. Cross-coupling of phenolic humus constituents and 2,4-dichlorophenol. Soil Sci. Soc. Am. J. 44:52-56.

Bollag, J.-M., and S.-Y. Liu. 1983. Incorporation of pentachlorophenol into humic acid polymers by a fungal laccase. p. 273. *In* Abstracts of the Annual Meeting of the ASM. Amer. Soc. Mocribiol., Wash., DC.

Bollag, J.-M., R.D. Minard, and S.-Y. Liu. 1983. Cross-linkage between anilines and phenolic humus constituents. Environ. Sci. Tech. 17:72-80.

Bonazountas, M., and J. Wagner. 1981. SESOIL — A seasonal soil compartment model. Arthur D. Little., Inc., Cambridge, Mass. Prepared for U.S. Environmental Protection Agency Office of Toxic Substances, Wash., D.C.

Botre, C., A. Memoli, and F. Alhaique. 1978. TCDD solubilization and photodecomposition in aqueous solutions. Environmental Science and Technology 12(3):335-336.

Bowers, W. 1970. Modern concepts of farm machinery management. Stipes Publishing Co., Champaign, IL.

Brady, N.C. 1974. The nature and properties of soil. Eighth edition. Macmillan Publishing Co., Inc., New York, NY.

Brandt, C.H. 1972. Soil physical property modifiers. *In* organic chemicals in the soil environment. Vol. 2. Goring, C.A.I., and Hamaker, J.W. (eds.). Marcel Dekker, Inc., New York, NY. pp 691-729

Breck, D.W. 1974. Zeolite molecular sieves, structure, chemistry, and use. Wiley Interscience. New York, NY.

Brown, D.P. 1978. Proposed volatile spill suppression concepts. pp. 303-308. *In* National Conference on Control of Hazardous Material Spills.

Brown, L.S. 1972. A physical barrier system for control of hazardous material spills in waterways. Proceedings of the 1972 National Conference on Control of Hazardous Material Spills, Houston, TX.

Brunner, W., and D.D. Focht. 1983. Persistence of polychlorinated phenyls (PCB) in soils under aerobic and anaerobic conditions. p. 266. *In* Abstracts of the annual meeting of the ASM. American Society for Microbiology, Wash., DC.

Bunce, N.J. 1982. Photodechlorination of PCB's: Current status. Chemosphere 11(8):701-714.

Burkhard, N., and J.A. Guth. 1979. Photolysis of organophosphorus insecticides on soil surfaces. Pest. Sci. 10:313.

Camoni, I., A. DiMuccio, D. Pontecovo, F. Taggi, and L. Vergoni. 1982. Laboratory investigation for microbiological degradation of 2,3,7,8-TCDD in soil by addition of organic compost. *In* Chlorinated dioxins and related compounds impact on the environment. Hutzinger, O. (ed.) Pergamon Press, New York, NY.

Cerniglia, C.E., and D.T. Gibson. 1979. Oxidation of benzo(a)pyrene by the filamentous fungus *Cunninghamella elegans*. J. Biol. Chem. 254(23):12174.

Cerniglia, C.E., R.L. Herbert, R.H. Dodge, P.J. Szaniszlo, and D.T. Gibson. 1979. Some approaches to studies on the degradation of aromatic hydrocarbons by fungi. *In* Microbial degradation of pollutants in marine environments. Bourquin, A.L., and Pritshard, H. (eds.). EPA-600/9-79-012, 360.

Chakrabarty, A.M. 1980. Plasmids and dissimilation of synthetic environmental pollutants. pp. 21-30. *In* Plasmids and transposons, environmental effects and maintenance mechanisms. Stuttard, C., and Rozee, K.R. (eds.). Academic Press, New York, NY.

Chakrabarty, A.M. 1982. Genetic mechanisms in the dissimilation of chlorinated compounds. pp. 127-139. *In* Biodegradation and detoxification of environmental pollutants, Chakrabarty, A.M. (ed.). CRC Press, Inc., Boca Raton, FL.

Chowdhury, A., D. Vockel, P.N. Moza, W. Klein, and F. Korte. 1981. Balance of conversion and degradation of 2,6-dichlorobenzonitrile - 14C in humus soil. Chemosphere 10:1101-1108.

Christensen, D.C., and W.C. Weimer. 1979. Enhanced photodegradation of persistent halogenated organic materials. Presented at the 34th Annual Purdue Industrial Waste Conference, Purdue University, Lafayette, IN., pp 160-166.

Coffey, D.L., and G.F. Warren. 1969. Inactivation of herbicides by activated carbon and other adsorbents. Weed Sci. 17:16-19.

Council for Agricultural Science and Technology (CAST). 1975. Utilization of animal manures and sewage sludges in food fiber production. Report No. 41.

Crosby, D.G. 1971. Environmental photooxidation of pesticides. pp 260-290. *In* Degradation of synthetic organic molecules in the biosphere. National Academy of Sciences, Wash., DC.

Crosby, D.G., A.S. Wong, J.R. Plimmer, and E.A. Woolson. 1971. Photodecomposition of chlorinated dibenzo-p-dioxins. Science 73:748.

Cupitt, L.T. 1980. Fate of toxic and hazardous materials in the air environment. EPA-600/53-80-084. U.S. Environmental Protection Agency, Athens, GA.

Damanakis, M., D.S. Drennan, J.D. Fryer, and K. Holly. 1970. The adsorption and mobility of praquat and different soil and soil constituents. Weed Res. 10:264-277.

David, D.J. 1978. Analysis of solids, plants, fertilizers, and other agricultural materials. Progress in Analytical Atomic Spectroscopy 1(3).

Dawson, G.W., B.W. Mercer, and C.H. Thompson. May 1980. Strategy for the treatment of spills on land. National Conference on Control of Hazardous Materials Spills.

Deere and Company. 1957. The operation, care and repair of farm machinery. 28th edition. Deere and Company, Moline, IL.

Department of the Army, Corps of Engineers. 1982. Preliminary guidelines for selection and design of remedial systems for uncontrolled hazardous waste sites. EM1110-2-(Draft). Department of the Army, Corps of Engineers, Wash., D.C.

Dobbs, R.A., and J.M. Cohen. 1980. Carbon adsorption isotherms for toxic organics. EPA-600/8-80-023. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH.

Donnan, W.W., and G.O. Schwab. 1974. Current drainage methods in the U.S.A. pp. 93-114. *In* Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. U.S. Forest Service General Technical Report NE-23, USDA — Forest Service, Upper Darby, PA.

Doyle, R.C., and J.D. Isbister. 1982. Treatment of TNT and RDX contaminated soils by composting. pp. 209-213. *In* Managing uncontrolled hazardous waste sites. Hazardous Materials Control Research Institute, Silver Spring, MD.

Dragun, J., and D.E. Baker. 1979. Electrochemistry. pp. 130-135. *In* The encyclopedia of soil science, Part I: Physics, chemistry, biology, fertility, and technology. Dowden Hutchinson, and Ross, Inc., Stroudsburg, PA.

Dragun, J., and C.S. Helling. 1982. Soil- and clay-catalyzed reactions: I. Physicochemical and structural relationships of organic chemicals undergoing free-radical oxidation. *In* Land disposal of hazardous waste. Proc. Eighth Annual Research Symposium. EPA-600/9-82-002.

Eckenfelder, Jr., W.W. 1970. Water quality engineering for practicing engineers. Barnes and Noble, Inc., New York, NY.

Edgehill, R.U., and R.K. Finn. 1983. Microbial treatment of soil to remove pentachlorophenol. Appl. Environ. Microbiol. 45:1122-1125.

Ehrenfeld, J.R., and J.M. Bass. 1983. Handbook for evaluating remedial action technology plans. U.S. Environmental Protection Agency, EPA-600/2-83-076, MERL, Cincinnati, OH.

Farmer, W.J., M.S. Yang, J. Letey, and W.F. Spencer. 1980. Land disposal of hexachlorobenzene wastes-controlling vapor movement in soils. EPA-600/2-80-119. Municipal Environmental Research Laboratory, ORD, U.S. EPA, Cincinnati, OH.

Finck, A. 1982. Fertilizers and fertilization. Verlag Chemie, Deerfield Beach, FL.

FMC Corporation. 1979. Industrial waste treatment with hydrogen peroxide. Industrial Chemicals Group, Phil., PA.

Focht, D.D., and M. Alexander. 1970. DOT metabolites and analogs: Ring fission by *Hydrogenomonas*. Science 170:91-92.

Follett, R.H., L.S. Murphy, and R.L. Donahue. 1981. Fertilizers and soil amendments. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Franklin Institute Research Laboratory, Inc., 1981. The Franklin Institute chemical method for detoxifying polychlorinated biphenyls (PCBs) and other toxic waste. Phila., PA.

Frink, C.R., and G.K. Voight. 1976. Potential effects of acid precipitation on soils in the humid temperature zone. pp. 685-709. *In* Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem. U.S. Forest Service General Technical Report NE-23, USDA — Forest Service, Upper Darby, PA.

Fry, A.W., and A.S. Grey. 1971. Sprinkler irrigation handbook. Rain Bird Sprinkler Mfg. Corporation, Glendora, CA.

Furukawa, K. 1982. Microbial degradation of polychlorinated biphenyls (PCBs). pp. 33-57. *In* Biodegradation and detoxification of environmental pollutants. Chakrabarty, A.M., (ed.). CRC Press, Boca Raton, FL.

Furukawa, T., and G.W. Brindley. 1973. Adsoption and oxidation of benzidine and aniline by montmorillonite and hectorite. Clay Miner. 21:279-288.

Graedel, T.E. 1978. Chemical compounds in the atmosphere. Academic Press, New York, NY.

Gray, T.R.G. 1978. Microbial aspects of the soil, plant, aquatic, air, and animal environments: Soil and plants. pp. 19-38. *In* Pesticide microbiology. Hill, I.R., and Wright, S.J.L. (eds.) Academic Press, New York, NY.

Greer, J.S., and S.S. Gross. 1980. The practicality of controlling vapor release from spills of volatile chemicals through cooling. pp. 130-133. *In* National Conference on Control of Hazardous Material Spills.

Griffin, R.A., and N.F. Shimp. 1978. Attenuation of pollutants in municipal landfill leachate by clay minerals. U.S. Environmental Protection Agency-600/2-78-157.

Grove, J.H., and B.G. Ellis. 1980. Extractable chromium as related to soil pH and applied chromium. Soil Sci. Soc. Am. J. 44:238-242.

Guidelines for data acquisition and data quality evaluation in environmental chemistry. 1980. Anal. Chem. 52:2242-2249.

Gupta, O.P. 1976. Adsorbents and antidotes. World Crops. 28:134-138.

Hautala, R. 1978. Surfactant effects on pesticide photochemistry in water and soil. EPA-600/3-78-060. U.S. Environmental Protection Agency, Athens, GA.

Hazardous Materials Control Research Institute. 1983. Hazardous Materials Control Directory, 1983-1984. Silver Spring, MD.

Henderson, R.W., G.R. Lightsey, and N.A. Poonawala. 1977b. Competitive adsorption of metal ions from solutions by low-cost organic materials. Nature 162:746-747.

Henderson, R.W., D.S. Andrews, G.R. Lightsey, and N.A. Poonawala. 1977a. Reduction of mercury, copper, nickel, cadmium, and zinc levels in solution by competitive adsorption onto peanut hulls, and raw and aged bark. Bull. Environ. Contam. Toxicol. 17:355-359.

Hendry, D.G., and R.A. Kenley. 1979. Atmospheric reaction products of organic compounds. Environmental Protection Agency Report EPA-560/12-79-001. 81p.

Hiltz, R. 1982. Vapor hazard control. pp. 10-21 to 10-33. *In* Hazardous Spills Handbook. Bennett, G.F., Featers, F.S. and Wilder, I. (eds.). McGraw-Hill Book Co., New York, NY.

Hirschler, A.E. 1966. Proton acids as electron acceptors on aluminosilicates. J. Catalysis 5:196-197.

Horowitz, A., J.M. Sulflita, and J.M. Tiedje. 1983. Reductive dehalogenation of halobenzoates by anaerobic lake sediment microorganisms. Appl. Environ. Microbiol. 45:1459-1465.

Huang, C.P., and F.B. Ostoric. 1978. The removal of cadmium(II) from dilute aqueous solution by activated carbon adsorption. J. Environ. Eng. Div., ASCE 104.

Huang, C.P., and E.H. Smith. 1981. Removal of cadmium(II) from plating waste water by an activated carbon process. *In* W.J. Cooper (ed.) Chemistry in water reuse, 2:355-400. Ann Arbor Sci. Publ., Ann Arbor, MI.

Implement and Tractor Red Book. 1983. Intertee Publishing Corp., Overland Park, KS.

Jacobs, L.W. 1977. Utilizing municipal sewage wastewaters and sludges on land for agricultural production. North Central Regional Extension Publication No. 52.

Jensen, R.A. 1982. United States industrial plans. *In* Hazardous materials spills handbook. Bennett, G.F., Feates, F.G., and Wilder, I. (eds.). McGraw-Hill Book Company, New York, NY. pp. 7-43 to 7-55.

Johnston, J.B., and S.B. Robinson. 1982. Opportunities for development of new detoxification processes through genetic engineering. pp. 301-314. *In* Detoxication of hazardous waste. Exner, J.H (ed.). Ann Arbor Science, Ann Arbor, MI.

JRB. 1982. Techniques for evaluating environmental processes associated with the land disposal of specific hazardous materials. Vol. I: Fundamentals. Report to U.S. Environmental Protection Agency.

JRB, Inc. 1982. Techniques for evaluating environmental processes associated with the land disposal of specific hazardous materials. II — Incompatible Wastes.

Jurinak, J.J., and N. Bauer. 1956. Thermodynamics of zinc adsorption on calcite, colomite, and magnesite-type minerals. Soil Sci. Soc. Am. Proc. 20:466-471.

Kaplan, D.L., and A.M. Kaplan. 1982a. Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions. Appl. Environ. Microbiol. 44:757-760.

Kaplan, D.L., and A.M. Kaplan 1982b. Composting industrial wastes — biochemical consideration. Biocycle May/June:42-44.

Khan, S.U. 1982. Studies on bound 14C-prometryn residues in soil and plants. Chemosphere 11:771-795.

Khan, S.U., and K.C. Iverson. 1982. Release of soil bound (non-extractable) residues by various physiological groups of microorganisms. J. Environ. Sci. Health B17:737-749.

Kilbane, J.J., D.K. Chatterjee, and A.M. Chakrabarty. 1983. Detoxification of 2,4,5-trichlorophenoxyacetic acid from contaminated soil by *Pseudomonas cepacia*. Appl. Environ. Microbiol. 45:1697-1700.

Kim, B.E. 1981. Treatment of metal containing wastewater with calcium sulfide. *In* Water-1980, AIChE 209 (77).

Kim, B.E. 1981. Treatment of metal containing wastewater with calcium sulfide. *In* Water-1980. AIChE (209) 77.

Kirk Othmer Encylopedia of Chemical Technology. 1982. Vol. 18. John Wiley & Sons, New York, NY.

Klopffer, W. Dec. 2-4, 1980. Rapid test for simulation of photo-oxidative degradation in the gas phase. *In* Int. Workshop on Test Methods and Assessing Procedures for the Determination of the Photochemical Degradation Behavior of Chemical Substances, Berlin.

Ko, W.H., and J.L. Lockwood. 1968. Accumulation and concentration of chlorinated hydrocarbon pesticides by micro-organisms in soil. Can. J. Microbiol. 14:1075-1078.

Kobayashi, H., and B.E. Rittman. 1982. Microbial removal of hazardous organic compounds. Environ. Sci. Technol. 16:170A-183A.

Konetzka, W.A. 1977. Microbiology of metal transformations. pp. 317-342. *In* Microorganisms and minerals. Weinberg, E.D. (ed.). Marcel Dekker, Inc., New York, NY.

Korte, N.E., J. Skopp, W.H. Fuller, E.E. Niebla, and B.A. Alesii. 1976. Trace element movement in soils influence of soil physical and chemical properties. Soil Sci. 121:350-359.

Kowalenko, C.G. 1978. Organic nitrogen, phosphorus and sulfur in soils. pp. 95-135. *In* Soil organic matter. Schnitzer, M. and Khan, S.U. (eds.). Elsevier Scientific Publishing Co., New York, NY.

Larsen, V.J., and H.H. Schierup. 1981. The use of straw for removal of heavy metals from wastewater. J. Environ. Qual. 10:188-193.

Lemaire, J., I. Campbell, H. Hulpke, J.A. Guth, W. Merz, L. Philip, and C. Von Waldow. 1982. An assessment of test methods for photodegradation of chemicals in the environment. Chemosphere 11(2):119-164.

Liang, L.N., J.L. Sinclair, L.M. Mallory, and M. Alexander. 1982. Fate in model ecosystems of microbial species of potential use in genetic engineering. Appl. Environ. Microbiol. 44:708-714.

Liberti, A., D. Broco, A. Allegrini, and G. Bertoni. 1978. Field photodegradation of TCDD by ultra-violet radiation. pp. 195-200. *In* Dioxin: Toxilogical and chemical aspects. Cattabeni, F., Cavallero, A., and Galli, G. (eds.). Spectrum Publications, Inc., New York, NY.

Lichtenstein, E.P., T.W. Fuhremann, and K.R. Schulz. 1968. Use of carbon to reduce the uptake of insecticidal soil residues by crop plants. J. Agr. Food Chem. 16:348-355.

Liu, S.-Y., R.D., Minard, and J.-M. Bollag. 1981. Coupling reactions of 2,4-dichlorophenol with various anilines. J. Agric. Food Chem. 29:253-257.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1982. Handbook of chemical property estimation methods. McGraw-Hill Book Company, New York, NY.

Mahmood, R., R. C. Sims. 1984. Management of toxic organic compounds in soil systems. Dissertation prepared for Utah State University, Dept. of Civil and Environmental Engineering. To be submitted August, 1984.

Marinucci, A.C., and R. Bartha. 1979. Biodegradation of 1,2,3- and 1,2,4-trichlorobenzene in soil and in liquid culture. Appl. Environ. Microbiol. 38:811-817.

Mattigod, S.W., G. Sposito, and A.L. Page. 1981. Factors affecting the solubility of trace metals in soils. *In* Chemistry in the Soil Environment, ASA Special Publication 40.

McBride, M.B. 1980. Chemisorption of Cd^{2+} on calcite surfaces. Soil Sci. Soc. Am. J. 44:26-28.

McBride, M.B. 1979. Chemisorption and precipitation of Mn^{2+} at $CaCO_3$ surfaces. Soil Sci. Soc. Am. J. 43:693-698.

McLean, E.O. 1982. Soil pH and lime requirement. pp. 199-224. *In* Methods of soil analysis. Part 2 — chemical and microbiological properties. Second Edition. Page, A.L. (ed.). American Society of Agronomy, Inc., Madison, WI.

McLean, E.O., S.W. Dumford, and F. Coronel. 1966. A comparison of several methods of determining lime requirements of soil. Soil Sci. Soc. Am. Proc. 30:26-30.

Mercer, B.W., A.J. Shuckrow, and L.L. Ames. 1970. Fixation of radioactive wastes in soil and salt cores with organic polymers. BNWL-1220.

Metry, A.A. 1980. The handbook of hazardous waste management. Technomic Publ., Westport, PA.

Meuser, J.M. and W.C. Wiemer. 1982. Amine-enhanced photodegradation of polychlorinated biphenyls. EPRI Research Project 1263-6. Battelle Pacific Northwest Laboratories.

Millington, R.J., and J.P. Quirk. 1961. Permeability of porous solids. Trans. Faraday Soc. 57:1200-1207.

Mulder, D. (ed.). 1979. Soil disinfection. Elsevier Scientific Publishing Co., Amsterdam.

Mulle, G.J. 1981. Chemical decomposition of PCBs in transformer fluids. The Acurex Process. Acurex Waste Technologies, Inc., Mountain View, CA.

Munnecke, D.M. 1980. Enzymatic detoxification of waste organophosphate pesticides. J. Agric. Food Chem. 28:105-111.

Munnecke, D.M., L.M. Johnson, H.W. Talbot, and S. Barik. 1982. Microbial metabolism and enzymology of selected pesticides. pp. 1-32. *In* Biodegradation and detoxification of environmental pollutants. Chakrabarty, A.M. (ed.). CRC Press, Inc., Boca Raton, FL.

Nagel, G., et al. 1982. Sanitation of groundwater by infiltration of ozone treated water. GWF-Wasser/Abwasser 123(8):399-407.

Nakayama, S., et al. Sept. 15, 1979. Ozone. Science and Engineering 1(2):119-132.

Nilles, G.P., and M.J. Zabik. 1975. Photochemistry of bioactive combasagran. J. Agr. Food Chem. 23:410.

Nimah, M.H., J. Ryan and M.A. Chaudhry. 1983. Effect of synthetic conditioners on soil water retention, hydraulic conductivity, pososity, and aggregation. Soil. Sci. Soc. Am. J. 47:742-745.

Occhiucci, G., and A. Patacchiola. 1982. Sensitized photodegradation of adsorbed polychlorobiphenyls (PCBs). Chemisphere 11(3):255-262.

O'Sullivan, D. 1981. Strong growth ahead for industrial enzymes. Chem. Eng. News 59(3):37-38.

Ou, L.-T., P.S.C. Rao, and J.M. Davidson. 1983. Methyl parathion degradation in soil: influence of soil-water tension. Soil Biol. Biochem. 15:211-215.

Overcash, M.R., and D. Pal. 1979. Design of land treatment systems for industrial wastes —theory and practice. Ann Arbor Science, Ann Arbor, MI.

Page, J.B. 1941. Unreadability of the benzidine color reactions as a test for montmorillonite. Soil Sci. 51:133-140.

Pal, D., J.B. Weber, and M.R. Overcash. 1980. Fate of polychlorinated biphenyls (PCBs) in soil-plant systems. Residue Reviews 74:45-98.

Peech, M. 1961. Lime requirements vs. soil pH curves for soils of New York State. Cornell University, Ithaca, NY.

Pfaender, F.K., and M. Alexander. 1972. Extensive microbial degradation of DDT in vitro and DDT metabolism by natural communities. J. Agric. Food Chem. 20:842-846.

Pillie, R.J., R.E. Baier, R.C. Ziegler, R.P. Lenard, J.C. Micholovic, S.L. Pek, and P.H. Bock. 1975. Methods to treat, control and monitor spilled hazardous materials. EPA-670/2-75-042.

Plimmer, J.R. 1971. Principles of photodecomposition of pesticides. pp. 279-290. *In* Degradation of synthetic organic molecules in the biosphere. National Academy of Sciences, Wash., D.C.

Plimmer, J.R., and U.I. Klingebiel. 1973. Photochemistry of dibenzo-p-dioxins. pp. 44-54. *In* Chlorodioxins — origin and fate. Blair, E.H. (ed.). American Chemical Society, Wash., DC.

Prengle, Jr., H.W. 1977. Evolution of the ozone/UV process for wastewater treatment. Presented at Seminar on Wastewater Treatment and Disinfection with Ozone. Cincinnati, OH. International Ozone Association, Vienna, VA.

Prior, L.A. 1975. Land availability, crop production, and fertilizer requirements in the United States. EPA/530/Sw-166. U.S. Environmental Protection Agency, Wash., D.C.

Purdue University. 1977. Soil characterization in Indiana: I. Field and laboratory procedures. Research Bulletin No. 943, Department of Agronomy.

Quastel, J.H., and P.G. Scholefield. 1953. Arsenite oxidation in soil. Soil Sci. 75:279-285.

Raymond, J.L., V.W. Jamison, and J.O. Hudson. 1976. Beneficial stimulation at bacterial activity in groundwaters containing petroleum products. AIChE, (73), 166:390-404.

Rice, R.G. 1981. Ozone for the treatment of hazardous materials. Water — 1980. Symposium series, American Institute of Chemical Engineers, 209 (77):79-107.

Santillan-Medrano, J., and J.J. Jurinak. 1975. The chemistry of lead and cadmium in soil solid phase formation. Soil Sci. Soc. Am. J. 39:851-856.

Saxena, A., and R. Bartha. 1983a. Modeling of the covalent attachment of chloroaniline residues to quinoidal sites of soil humus. Bull. Environ. Contam. Toxicol. 30:485-491.

Saxena, A., and R. Bartha. 1983b. Microbial mineralization of humic acid — 3,4-dichloroaniline complexes. Soil Biol. Biochem. 15:59-62.

Saxena, J., and P.H. Howard. 1977. Environmental transformation of alkylated and inorganic forms of certain metals. pp. 185-226. *In* Advances in applied microbiology., Perlman, D. (ed.). Academic Press, New York, NY.

Schilfgaarde, J.V. 1974. Drainage for agriculture. Agronomy Monograph No. 17, Amer. Soc. of Agron., Inc., Madison, WI.

Schwab, G.O., R.K. Frevert, T.W. Edminster, and K.K. Barhes. 1981. Soil and water conservation engineering. Third edition. John Wiley and Sons, New York, NY.

Sharma, S., and R. Singh. 1983. Selenium in soil, plant, and animal systems. CRC Critical Reviews in Environmental Control 13(1):23-50.

Sherman, J.D. 1978. Ion exchange separation with molecular sieve zeolites. *In* Adsorption and Ion Exchange Separation. Sherman, J.D. (ed.). AIChE Symposium Ser. No. 179:98-116.

Shin, Y., J.J. Chodan, and A.R. Wolcott. 1970. Adsorption of DDT by soils, soil fractions, and biological materials. J. Agr. Food Chem. 18:1129-1133.

Shippen, J.M., C.R. Ellin, and C.H. Clover. 1980. Basic farm machinery. Third edition. Pergamon Press, New York, NY.

Sikora, L.J., D.D. Kaufman, M.A. Ramirez, and G.B. Willson. March 8-10, 1982. Degradation of pentachlorophenol and pentachloronitrobenzene in a laboratory composting system. *In* Proc. Eighth Ann. Symp. on Disposal of Hazardous Wastes. U.S. Environmental Protection Agency, Cincinnati, OH

Sims, R.C., and M.R. Overcash. 1981. Land treatment of coal conversion wastewaters. *In* Environmental aspects of coal conversion technology VI, a symposium on coal-based synfuels. EPA-600/9-82-017. U.S. Environmental Protection Agency, Wash., DC.

Sims, R.C. and M. Overcash. 1983. Fate of polynuclear aromatic compounds (PNAs) in soil-plant systems. Residue Reviews 88:1-68.

Sjobland, R.D., and J.-M. Bollag. 1981. Oxidative coupling of aromatic compounds by enzymes from soil microorganisms. pp. 113-152. *In* Soil biochemistry. Vol. 5. Paul, E.A., and Ladd, J.N. (eds.). Marcel Dekker, Inc., New York, NY.

Skujins, J., S.O. McDonald, and W.G. Knight. 1983. Metal ion availability during biodegradation of waste oil in semi-arid soils. Environmental Biogeochemistry 35:341-350.

Smeulders, F., A. Maes, J. Sinnaeve, and A. Cremers. 1983. In situ immobilization of heavy metals with tetraethylenepentamine (tetren) in natural soils and its effect on toxicity and plant growth. Plant and Soils. 70:37-47.

Soil Conservation Service. 1972. Soil survey laboratory methods and procedures for collecting soil samples. Soil Survey Investigation Report No. 1, U.S. Department of Agriculture, Wash., D.C.

Soil Conservation Service. 1979. Guide for sediment control on construction sites in North Carolina. U.S. Dept. of Agriculture, Soil Conservation Service, Raleigh, NC.

Solomon, D.H. 1968. Clay minerals as electron acceptors and/or electron donors in organic reactions. Clay Miner. 16:31-39.

Sommers, L.E., C.M. Gilmour R.E. Wildung, and S.M. Beck. 1981. The effect of water potential on decomposition processes in soils. pp. 97-117. *In* Water potential relations in soil microbiology. SSA Special Publication Number 9, Soil Sci. Soc. of Amer., Madison, WI.

Spencer, W.F., J.D. Adam, T.D. Shoup, and R.C. Spear. 1980. Conversion of parathion to paraoxon on soil dusts and clay minerals as affected by ozone and UV light. J. Agr. Food Chem. 28:369.

Staiff, D.C., L.C. Butler, and J.E. Davis. 1981. A field study of the chemical degradation of paraquat dichloride following simulated spillage on soil. Bull. Environ. Contam. Toxicol. 26:16-21.

Stevenson, F.J. 1972. Role and function of humus in soil with emphasis on adsorption of herbicides and chelation of micronutrients. Bioscience 22(11):643-650.

Stotsky, G., and V.N. Krasovsky. 1981. Ecological factors that affect the survival, establishment, growth, and genetic recombination of microbes in natural habitats. pp. 31-42. *In* molecular biology, pathogenicity and ecology of bacterial plasmids. Levy, S.F., Clowes, R.C., and Koenig E.L. (eds.). Plenum Press, New York, NY.

Strek, H.J., J.B. Weber, P.J. Shea, E. Mrozek, Jr., and M.R. Overcash. 1981. Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon. J. Agr. Food Chem. 29:288-293.

Sulflita, J.M., and J.-M. Bollag. 1980. Oxidative coupling activity in soil extracts. Soil Viol. Biochem. 12:177-183.

Sulflita, J.M., A. Horowitz, D.R. Shelton, and J.M. Tiedje. 1982. Dehalogenation: a novel pathway for the anaerobic biodegradation of haloaromatic compounds. Science 218:1115-1117.

Sulflita, J.M., J.A. Robinson, and J.M. Tiedje. 1983. Kinetics of microbial dehalogenation of haloaromatic substrates in methanogenic environments. Appl. Environ. Microbiol. 45:1466-1473.

Sulflita, J.M., and J.M. Tiedje. 1983. The anaerobic degradation of 2,4,5-trichlorophenoxyacetic acid by a dehalogenating bacterial consortium. p. 266. *In* Abstracts of the Annual Meeting of the ASM. Amer. Soc. for Microbiol., Wash., D.C.

Sweeney, K. 1981. Reductive treatment of industrial wastewaters. I. Process and description and II. Process application. pp. 67-78. *In* Water 1980. G.F. Bennett (ed.). American Institute of Chemical Engineers Symposium, Series 209 (77).

Tames, R.S., and R.J. Hance. 1969. The adsorption of herbicides by roots. Plant and Soil. 30:221-226.

Taylor, J.M., J.F. Parr, L.J. Sidora, and G.B. Wilson. 1980. Consideration in the land treatment of hazardous wastes: Principles and practices. *In* 2nd Oil and Hazardous Spills Conference and Exhibition.

Taylor, S.A., and G.L. Ashcroft. 1972. Physical Edaphology. W.H. Freeman and Co., San Francisco, CA. 533 p.

Theng, B.K.G. 1974. The chemistry of clay-oganic reactions. Adam Hilger, London.

Thibault, G.T., and N.W. Elliott. 1980. Biological detoxification of hazardous organic chemical spills. pp. 398-402. *In* Control of hazardous material spills. Vanderbilt University, Nashville, TN.

Thibault, G.T., and N.W. Elliott. 1979. Accelerating the biological clean-up of hazardous materials spills. pp. 115-120. *In* Oil and hazardous material spills: Prevention-control-cleanup-recovery-disposal. Information transfer, Inc., Silver Spring, MD.

Thibodeaux, L.J., and S.T. Hwang. 1982. Landfarming of petroleum wastes modeling the air emission problem. Env. Progress 1(1):42-46.

Turner, J.H., and C.L. Anderson, 1980. Planning for an irrigation system. American Association for Vocational Instruction Materials, Athens, GA.

U.S. Environmental Protection Agency. 1976. Application of sewage sludge to cropland: Appraisal of potential hazards of the heavy metals to plants and animals. MCD — 33 EPA 430/9-76-013.

U.S. Environmental Protection Agency. 1977. Environmental assessment of subsurface disposal of municipal wastewater treatment sludge. Interim report. EPA/530/SW-547.

U.S. Environmental Protection Agency. 1977. Municipal sludge management: Environmental factors. MCD-28. EPA 430/9-9-77-004.

U.S. Environmental Protection Agency. 1978. Municipal sludge agricultural utilization practices. An environmental assessment. 1: SW-709.

U.S. Environmental Protection Agency. 1978. Applications of sludges and wastewaters on agricultural land: A planning and educational guide. MCD-35.

U.S. Environmental Protection Agency. 1980. A guide to regulations and guidance for utilization and disposal of municipal sludge. MCD-72. EPA 430/9-80-015.

U.S. Environmental Protection Agency. 1981. Effects of sewage sludge on the cadmium and zinc content of crops. EPA-600/8-81-003.

U.S. Environmental Protection Agency. 1982. Handbook for remedial action at waste disposal sites. EPA-625/6-82-006. Municipal Environmental Research Laboratory, Office of Research and Development. Wash., D.C.

U.S. Environmental Protection Agency. 1982. Test methods for evaluating solid waste. SW-846, 2nd Ed.

U.S. Environmental Protection Agency. 1983. Hazardous waste land treatment. SW-874 (Revised edition). Wash., D.C.

Voerman, S., and P.M. Tammes. 1969. Adsorption and desorption of lindane and dieldrin by yeast. Bull. Environ. Contam. Toxicol. 4:271-277.

Walker, A., and D.V. Crawford. 1968. The role of organic matter in adsorption of the triazine herbicides by soil. *In* Isotopes and radiation in soil organic matter studies. Proc. 2nd Symp. Int. Atomic Energy Agency. Vienna, Austria.

Wallnöfer, P.R., W. Ziegler, and G. Engelhardt. 1981. Bacterial oxidation of 4-methylthio-substituted veratrylglycerol-B-aryl-ethers, model compounds for soil bound pesticide residues. Chemosphere 10:341-346.

Walsh, L.M., and J.D. Beaton (ed.). 1973. Soil testing and plant analysis. Soil. Sci. Soc. Amer., Inc., Madison, WI.

Walton, G.C., and D. Dobbs. 1980. Biodegradation of hazardous materials in spill situations. pp. 23-29. *In* Control of hazardous material spills. Vanderbilt University, Nashville, TN.

Weast, R.C., 1983. Handbook of chemistry and physics. CRC Press, Cleveland, OH.

Weber, J.B., and E. Mrozek, Jr. 1979. Polychlorinated biphenyls: Phytotoxicity, adsorption and translocation by plants, and inactivation by activated carbon. Bull. Environ. Contam. Toxicol. 23:412-417.

Weber, J.B., P.W. Perry, and R.P. Upchurch. 1965. The influence of temperature and time of the adsorption of paraquat, diquat, 2,4-D, and prometone by clays, charcoal, and an anion exchange resin. Soil Sci. Soc. Am. Proc. 29:678-688.

Williams, E.B. May 26-28, 1982. Contamination containment by in-situ polymerization. Second National Symposium on Aquifer Restoration and Groundwater Monitoring. National Water Well Association. Worthington, OH.

Wilson, L.G. 1980. Monitoring in the vadose zone: A review of technical elements and methods. EPA-600/7-80/134. U.S. Environmental Protection Agency, Las Vegas, NV.

Wipf, H.K., E. Homberger, N. Neuner, and F. Schenker. 1978. Field trials on photodegradation of TCDD on vegetation after spraying with vegetable oil. pp. 201-217. *In* Dioxin: Toxilogical and chemical aspects. Cattabeni, F., Cavallero, A., and Galli, G. (eds.). Spectrum Publications, Inc., New York, NY.

Woodrow, J.E., D.G. Crosby, and J.N. Seiber. 1983. Vapor-phase photochemistry of pesticides. Residue Reviews 85:111-125.

Woolson, E.A. 1977. Fate of arsenicals in different environmental substrates. Environ. Health Perspect. 19:73-81.

Yagi, O., and R. Sudo. 1980. Degradation of polychlorinated biphenyls by microorganisms. JWPCF. 52:1035-1043.

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- Zinc powder, as reducing agent, 5, 76, 77, 78, 78t

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